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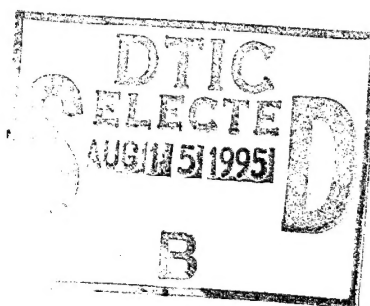
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UNITED STATES ATOMIC ENERGY COMMISSION

HIGH DENSITY GRAPHITE

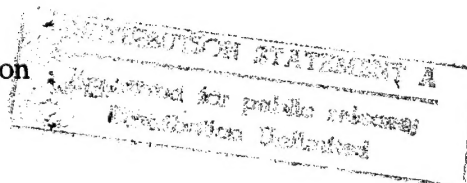
Final Report

By  
M. W. Nathans



September 2, 1954

Great Lakes Carbon Corporation  
Morton Grove, Illinois



Technical Information Service, Oak Ridge, Tennessee



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Work performed under Contract No. AT(11-1)-221.

Research and Development Division  
Great Lakes Carbon Corporation  
Morton Grove, Illinois

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## I. ABSTRACT

### Scope:

1. Develop a sequence of conventional operations in the preparation of synthetic graphite of a density of 2.00 and above in which sequence the effect of each operation is maximized.
2. Modify and improve present processes and develop new techniques which are beneficial to the preparation of high density graphite.
3. Analyze the products to determine the conditions best applicable to producing the highest density graphite possible with the highest strength characteristics.

### Program:

#### A. Conventional Methods

A sequence of conventional operations was developed for the preparation of high density extruded stock. During the course of this development the following unit operations were examined with a view towards maximizing their contributions to the density of the final product.

#### Formulation:

The addition of various amounts of carbon black to the usual petroleum coke - coal tar pitch binder mix.

#### Forming:

Molding as compared to extrusion.

#### Baking:

The effect of mix formulation on the volumetric shrinkage and binder coke residue; the effect of adding organic carbon residue promoters on the binder coke residue and the shrinkage; the effects of baking under mechanical or pneumatic superatmospheric pressures.

#### Impregnation:

The effect of the number of impregnations on the density of the baked stock and of the graphitized product; the impregnability of stock baked under atmospheric and super-atmospheric pressure.

#### Graphitization:

The effect of the upheal rate on the volumetric shrinkage, and hence the density of the final product.

#### Purification:

The applicability of the F process to the high density materials being prepared.

### B. Unconventional Methods

High density briquetted stock was prepared by the application of a number of unconventional processes.

#### Formulation:

Flake graphite instead of calcined or graphitized petroleum coke; polymeric, preferably three-dimensional thermosetting binders instead of coal tar pitch binder; binder-free systems.

#### Forming:

The use of a regular mold or a split mold; molding at various temperatures followed by ejection at room temperature as well as at elevated temperatures;

#### Baking (Carbonization of the Binder):

Conventional atmospheric baking compared to baking under mechanical pressure.

#### Densification:

The deposition of carbon from a gas phase in the pores of the graphite by means of the pyrolytic decomposition of hydrocarbon gases.

#### Purification:

Removal of ash by the F process applied to the base-graphite before molding; removal of residual hydrogen after carbon deposition by heat treatment of the densified briquettes; the effect of the heat treatment on the density and the volumetric expansion of the briquettes.

## Summary of Results

### High Density Graphite from Petroleum Coke

Graphite of 2.00 density has been produced by conventional processing techniques, starting with a composition consisting of 65 parts petroleum coke flour, 35 parts Thermax and 31 parts coal tar pitch binder. The sequence of operations is as follows: Extruded specimens are baked under atmospheric pressure, impregnated with a single phase pitch (softening point 85 to 90° C), rebaked under atmospheric pressure and graphitized to 2900° C at a rate not exceeding 0.5° C per hour in the critical range of 1300° to 2100° C. The graphitized piece is impregnated a second time, rebaked and finally regraphitized. A simplified flow diagram of the process is given in Figure 1.

With the particular coke employed in this work, extruded stock yielded considerably higher densities than molded stock.

The incorporation of carbon black in the mix was essential to the attainment of a high density, since it greatly enhances the shrinkage during baking and graphitization. Organic carbon residue promoters such as polyvinyl chloride increased the binder coke yield, but had an undesirable effect on the volumetric shrinkage during heat treatment and were, therefore, of no value in the preparation of high density graphite.

The binder coke residue was found to be independent of the carbon black/coke flour ratio but decreased with increasing binder level to a constant value. On the other hand, the volumetric shrinkage increased with an increase of the carbon black/coke flour ratio.

Mechanical pressure baking offered no advantages over either atmospheric baking or pneumatic pressure baking. Pneumatic pressure baking increased both the binder coke residue and the density compared to conventional baking. However, pressure baked stock was less amenable to pitch impregnation than conventionally baked stock. The net effect of baking under pneumatic pressure was, therefore, negligible.

Exhaustive impregnation of baked stock increased the final density in the baked state, but decreased the volumetric shrinkage upon subsequent graphitization. The densities in the graphitized state showed a maximum when only one impregnation was used in the process.

In order to obtain the maximum shrinkage during graphitization, it was necessary to employ a slow graphitization rate, of the order of 30° C per hour between 1300° C and 2100° C and 60° C per hour below 1300° and above 2100° C.

Some densification could be achieved by means of gaseous deposition with the high density extruded stock. The process was most efficient, though slow, with graphitized material which had not been subjected to pitch impregnation at any time. With all other high density extruded stock the deposition rates were too slow to be of any practical consequence. This fact can be attributed to the distribution and the nature of the pores which prevented a sufficiently fast rate of diffusion of the gas into the pores.



The F process could not be applied directly to the preparation of purified high density graphite, probably for the same reason as experienced with gaseous deposition.

#### High Density Graphite from Natural Graphite

Graphite of density 2.01 - 2.03 has been prepared by molding purified Superflake graphite under 6000 psi pressure at room temperature and then binding the particles with simultaneous densification by means of the pyrolytic decomposition of propane gas at 700° C. Removal of residual hydrogen is effected by heating the pieces to 2000° C at a rate not exceeding 40° C per hour. Methane gas at 900° C can be used instead of propane at 700° C for the gaseous deposition. The lower required temperature makes propane more suitable, however.

Three-dimensional polymeric binders could be used during molding, when the binder was allowed to set in the mold. Carbonization of the binder could be effected either in the mold under pressure or by conventional methods. Lamination during ejection was found to be a major problem, however.

Heat treatment of densified flake graphite briquettes for the removal of residual hydrogen was accompanied by an initial shrinkage up to about 1200° C after which the briquettes expanded. The loss of density due to the heat treatment was only of the order of 0.01 - 0.02 g/cc.

### Properties

The properties of the high density extruded stock are listed below:

Apparent Density, g/cc	1.95 - 2.01	
Elastic Modulus, psi x 10 <sup>6</sup>	2.8 - 3.3	
Crushing strength, psi, Transverse	3400 ± 1400	1)
Axial	8800 ± 700	2)
Cross Breaking Strength, psi		
Transverse	(1300)	3)
Axial	4000 ± 500	2)
Coefficient of Thermal Expansion, °C <sup>-1</sup> x 10 <sup>6</sup>		
Transverse	6.1	
Axial	3.4	2)
Electrical Resistivity, ohm in. x 10 <sup>-4</sup>		
Transverse	10.1	1)
Axial	4.25	2)
Ash, %	0.01	

- 1) Average of three determinations.
- 2) Average of two determinations.
- 3) Specimen showed cracks before testing.

The material is highly anisotropic. On sectioning, the pieces exhibited some flaws which had their origin in the extrusion and baking operations.

### Recommendations:

The internal structure of the extruded high density stock has emphasized the fact that a number of technical problems are yet to be solved. These problems are primarily in the realm of the extrusion and baking of high density compositions. Furthermore, it is to be expected that additional problems may arise when the methods developed here are applied to the manufacture of larger

pieces. Finally, before reactor grade graphite of such high density can become a reality, a substitute for or a modification of the F process will have to be developed.

## II. INTRODUCTION

Under previous agreements, (Contracts AT(45-1)-269 and AT(11-1)-172) between Great Lakes Carbon Corporation and the Atomic Energy Commission, it was found that a number of petroleum cokes could be successfully purified by means of a purification process which reduced the ash content of synthetic graphite to a level which contributed no more than about 0.08 mb to the neutron absorption cross-section of the graphite. Thus, one of the factors governing the suitability of graphite as a reactor material had been thoroughly investigated.

Another important factor to be considered in reactor grade graphite is the apparent density, since the efficiency of graphite as a moderator depends on it. If the density of reactor graphite could be increased to 2.00 or above, a reduction in the physical size of at least 15 to 20% would be possible with an additional bonus, if higher densities could be obtained.

The present contract, No. AT(11-1)-221, was drawn up for the express purpose of developing such high density graphite.

### III. SCOPE OF THE WORK

Under the terms of the contract No. AT(11-1)-221 (Juel) Great Lakes Carbon agreed to conduct research and development to improve methods and operations of preparing synthetic graphite of reactor quality with an apparent density approaching that of real graphite. The work was to include:

1. The development of a sequence of conventional operations in the preparation of synthetic graphite in which each operation produces the nearest to maximum effects at that stage of the process.
2. The modification of present processes by the introduction of new techniques to obtain improvement of normal processing operations employed in the preparation of high coking value binder, impregnating agents, low porosity carbon and high density synthetic graphite.
3. The analysis of resulting products to determine the conditions best applicable to producing graphite with maximum possible density and strength characteristics occurring simultaneously.

In addition, provision was made for tests of the materials produced at a place and in a manner to be designated by the Commission.

#### IV. PHYSICAL FACILITIES

The physical facilities provided at Morton Grove under the previous contracts No. AT(45-1)-269 and No. AT(11-1)-172 were adequate for conducting the present investigations after a general reconditioning had taken place.

#### V. EQUIPMENT AND PROCESSING

The equipment used for the mixing, extrusion, atmospheric baking and graphitizing of extruded stock was that which is normally part of the facilities at Morton Grove.

The purification unit which was used once or twice was the same unit used during the previous contract. No repairs or modifications other than the replacement of the graphite resistance tube was required. An autoclave for pressure impregnation was also available.

Another autoclave was purchased for pneumatic pressure baking experiments.\*

An ordinary mold and a split mold were designed \*\* for the purpose of pressing graphite aggregates with and without dimensional polymeric binders. Heating jackets for these molds were constructed to allow mechanical pressure baking.

\* For drawings: See June - November, 1952 report.  
For picture, diagram: See March - May 1953 report, No. C00-137.

For drawings: Regular mold, See June - November, 1952 report.  
Split Mold, See December 1953 - February 1954  
report, No. C00-201.

Two tubular furnaces, in which gaseous deposition experiments were to be run, were constructed. The smaller one was a 2 kVA Globar furnace with a 2 3/8" x 36" tube and was used for the treatment of small pressed specimens. The larger one was a resistance wound 1.25 kVA furnace with a 3 1/4" diameter x 51" tube and was used for the treatment of extruded stock and large pressed specimens.

The techniques used in the manufacture and processing of extruded stock were those of conventional practice.

The techniques used in the preparation of graphite aggregates bonded with polymeric binders were varied as our experience in this phase of the work increased and will be further discussed in the appropriate place.

Gaseous impregnation experiments were carried out by leading the gas (methane or propane) past the specimen in a heated furnace at a flow rate of approximately 12 liters/hr. The specimen temperature was maintained between 690° and 705° C. with propane and between 900° and 910° C with methane.

## VI. RAW MATERIALS AND THEIR PREPARATION FOR USE

### A. Low Porosity Carbon

#### 1. Petroleum Coke

Two types of closely related petroleum cokes were used. No size reduction was necessary since nearly all passed a 48 mesh sieve. Their properties are:

	I	II
Sample Identification	1249-MG-745	253-MG-15
Real density, g/cc	2.106	2.094
A D of particles	1.65	--
Sulfur, %	0.34	0.15 - 0.2
Ash, %	0.27	0.2
Sieve Analysis (%)		
+48	5.4	2.4
48/200	49	29
-200	43	68

Coke I was used in all experiments except the last two extrusions which were carried out with Coke II.

#### 2. Thermax

This is a furnace black with the following properties:

Real Density, g/cc	1.938
Total volatiles, %	0.40
Particle size, millimicrons	275

### 3. Kish

This is a type of flake graphite precipitated from molten iron. The impure material contained:

Ash, %	23.4
Iron, %	9.76

After leaching in 6N HCl and three washings in hot distilled water, it contained:

Ash, %	6.43
Iron, %	0.20

### 4. Superflake Graphite (Natural Graphite)

This graphite was obtained from Superior Graphite Company. Grade 198 was used in the "as received" state, when purified by simple heat treatment and purified by the F process. The ash contents were:

Unpurified	0.49% (4900 ppm)
Heat treated	0.002 - 0.004% (20 - 40 ppm)
Purified by F process	0.0006% (6 ppm)

### B. Coal Tar Pitch Binder

The binder was a pitch containing ca 30% benzene insoluble fraction and having a softening point of about 100° C (30 Medium pitch, Barrett's designation). Analysis showed the following properties:

Softening point, °C	1) 102
Specific gravity at 25° C.	2) 1.315
Benzene insoluble, %	3) 27.0
Quinoline insoluble, %	4) 13.2

After carbonization and baking to 900° C.

Real density, g/cc	1.930
--------------------	-------

- 1) Barrett test No. D-7
- 2) Barrett test No. B-5
- 3) Barrett test No. B-7
- 4) Barrett test No. PC-169



C. Impregnating Agents

Several materials were used as impregnants.

1. Koppers' pitch oil (a by-product oil from the coking of coal tar pitch in slot ovens) was filtered, topped at 300° C. and vacuum distilled. The properties of the resulting material are:

Softening point, °C	82
Specific gravity at 25°C	1.264
Benzene insoluble, %	3.7
Quinoline insoluble, %	0.05

2. Resin "C" pitch (a fraction from a distillation of coal tar pitch obtained from the Barrett Company) was filtered, topped and vacuum distilled. The properties of the resulting material are:

Softening point, °C	93.0
Specific gravity at 25°C	1.281

3. In one or two instances an impregnation was made with a pitch containing ca 15% benzene insoluble fraction, which was the residue from a vacuum distillation of coal tar pitch and had a softening point of about 100° C. (15 vacuum pitch (Barrett Company's designation). Its measured properties are:

Softening point, °C	106
Specific gravity at 25°C	1.266

## VII. PRESENTATION AND DISCUSSION OF RESULTS

In the proposal upon which the present contract AT(11-1)-221 is based, a generalized flow diagram for the production of high density graphite was presented. (Figure 2). The greater part of the work performed under the contract has followed this diagram, whereby the effect of each step, alone or in combination with other steps, has been maximized simply by the efficient use and choice of conventional processes.

### A. Molded Stock

#### A 1 Formulation

Two systems have been investigated, viz. (a) a system consisting of calcined petroleum coke flour possessing a low porosity, carbon black (Thermax, in this instance) and a two-phase coal tar pitch binder and (b) a system consisting only of petroleum coke flour and a coal tar pitch binder.

#### a. The Three-component System

For the investigation of this system, a number of mixes were prepared in which both the ratio of coke flour to carbon black and the binder content were varied. Experimental specimens were molded, baked and graphitized. The results are shown graphically in Figures 3 and 4.

It can be seen that, in general, the apparent densities in the corresponding green, baked and graphitized states occur at about the same binder level. This results from the fact that an increase in the volumetric shrinkage compensates a decrease in the binder coke residue (cf Section A 3).

Figure 5 shows the total volume shrinkage between the green and graphitized states as a function of the binder content. The maxima in these curves occur at a higher binder content than the density curves. This difference is caused by the continuous decrease in the binder coke residue (cf Section A 3).

From the curves in Figure 4 the optimum amount of binder was established at 26, 28, and 29 parts per 100 parts of 85/15, 75/25 and 65/35 coke flour/Thermax aggregate respectively.

Figure 6 is a plot of the apparent density of the graphitized specimens as a function of the Thermax content of the base coke for the optimum amount of binder. One can see that a maximum in density is reached at about 35% Thermax.

b. The Two-component System

The coke flour-pitch binder system was investigated because the poor graphitizing qualities of carbon blacks would tend to lower the theoretical maximum density. The effect of the only variable in this system, the binder content of the mix, was investigated in the same way as in the three component system. Figure 7 shows the apparent densities of a series of molded specimens in the green, baked and graphitized states. Figure 8 shows the volume shrinkage of the specimens during graphitization. It is seen that the apparent densities of the baked and graphitized specimens are only slightly affected by variations in the binder content. The large dip in the curve of Figure 8 between a binder content of 35 parts and 40 parts has been attributed to the existence of insufficient porosity to accommodate the decomposition gases and the

resulting expansion caused by these gases being under pressure. The optimum binder content appears to be 36 parts binder per 100 parts coke flour.

#### A 2 Mixing

In preparing mixes involving Thermax it was observed that after about twenty minutes the mix was converted into discrete balls of uniform size, which did not fuse together upon molding. This condition was attributed to the type of mixing action obtained in the laboratory dough-type intensive mixer with sigma blades. Milling the cooled mix prior to molding improved the appearance of the molded specimens but did not improve the density of the graphitized specimens.

It is to be pointed out that the agglomeration would be much less objectionable in extrusion since the relative motion of the particles in extrusion is much greater than in molding.

#### A 3 Baking

The baking operation is a very important step in the preparation of high density graphite, since during baking a permanent structure is given to the carbon through the formation of coke bridges between the constituent particles of the base coke. The baking operation should be designed so as to give the largest possible binder coke yield with the largest possible shrinkage.

Since the binder coke residue under a given set of baking conditions is affected by the base coke composition and by the external pressure, and also can be increased by the

use of certain additives, these three factors were investigated separately.

a. Variation in Binder Coke Residue with Binder Level and Thermax Content

The data obtained in this investigation are summarized in Table I. The binder coke residue is independent of the coke flour/Thermax ratio, but decreases with increasing binder level to a constant value at about 28 parts binder per 100 parts of carbon. The accompanying effect on the densities of the baked and graphitized specimens has been discussed in Section A 1 on Formulation.

TABLE I

Variation in Binder Coke Residue with Binder Level

Base Components Coke Flour/Thermax	Binder Content Parts/100 of Carbon	Coke Residue from Binder %	
		Bake #1	Bake #2
85/15	20	76	
	23	67.5	
	26	68	
	28		64
	30		64
	32		61.5
75/25	21	76	
	24	68.5	
	27	68	64
	29		65
	31		62
	33		65
65/35	23	75	
	26	67.5	
	29	69	62
	31		64
	33		64
	35		65

TABLE II  
Effect of Polyvinyl Chloride on Coke Residue

Material	Polyvinyl Chloride %	Coke Residue %	Increase in Coke Residue due to PVC
Resin C	None	58.8	-
Resin C	2.0	65.1	6.3
Koppers Pitch Oil, filtered and topped to 425° C	None	62.0	-
Koppers Pitch Oil, filtered and topped to 425° C	2.0	69.4	7.4
15 - Vacuum Pitch, filtered	None	67.6	-
15 - Vacuum Pitch, filtered	2.0	72.5	4.9
Resin C, vacuum distilled	None	65.2	-
Resin C, vacuum distilled	2.0	72.1	6.9
Koppers Pitch Oil, filtered, vacuum distilled	None	70.4	-
Koppers Pitch Oil, filtered, vacuum distilled	2.0	76.0	5.6

TABLE III  
Effect of Polyvinyl Chloride as a Promoter of Density

PVC * in binder %	0	0.5	1.5	3.0
Apparent Density, green	1.78	1.77	1.78	1.77
Apparent Density, baked	1.73	1.73	1.74	1.72
Volume change %	-1.3	-1.2	-0.8	-0.9
Carbon residue from Binder %	80.1	84.7	84.6	83.8

\* PVC - polyvinyl chloride.

b. Effect of Additives upon the Yield of Coke  
from Pitches and Pitch Fractions

Additives in the form of oxidizing agents, dehydrogenating agents or agents that will, by chemical or physical means, raise the volatilization temperatures of the pitch components above their decomposition temperatures will usually increase the coke yield of a pitch. For this reason a few experiments were made in which polyvinyl chloride (PVC) was added to the binder or the impregnating agent, and in which these pitches were subsequently coked by heating in containers over the normal baking cycle (see below). The results with impregnants are summarized in Table II. A 2% addition of PVC increases the coke yield about 6% for all pitches investigated. Incorporating PVC in the binder has no effect on the density of baked pieces, however, as is clear from Table III. The increase in coke residue is effected by a decrease in volumetric shrinkage.

TABLE IV  
Processing Data of Pressed Kish-Binder Systems

Sample No.	Composition Kish Binder Parts by Weight	A D Green	Baking Conditions	A D Baked	A D Graph.	Weight Loss Bake- Graph. %	$\Delta$ V Bake- Graph. %	A D Graph. (Using baked wt.)
ACS-2	100 <sup>1</sup>	1.78	Conventional <sup>2</sup>	1.61	1.23	—	—	—
ACS-3	25 <sup>3</sup>	1.87	Mechanical <sup>4</sup>	2.07	1.35	33.6	1.6	2.03
AC8-1	100 <sup>5</sup>	—	Mechanical <sup>6</sup>	1.73	1.45	13.3	2.6	1.68
AC8-2	"	—	"	1.82	1.59	10.7	2.1	1.78
AC8-3	"	—	"	1.84	1.61	10.8	1.3	1.82
AC8-4	"	—	"	1.84	1.62	10.8	1.0	1.82

- 1 - Refers to impure Kish: Ash = 23.4%, Fe = 9.76%.
- 2 - Indicates 900°C maximum temperature @ 150°C/day rate of upheat.
- 3 - Includes 1.5 parts polyvinyl chloride.
- 4 - Indicates 5000 psi mechanical pressure while heating to 550° C @ 65°C/hr.
- 5 - Refers to HCl treated Kish: Ash = 6.43%, Fe = 0.2%.
- 6 - Pressed @ 5000 psi through 250°C; 3500 psi through 400° C; 2000 psi through 550° C.



### c. Pressure Baking

When the binder is carbonized during baking, the escaping volatiles develop an internal pressure in the piece causing the latter to expand. This expansion will become permanent as soon as the binder has passed the plastic stage and is carbonized. As a means of preventing the expansion and thereby of obtaining a higher density of packing the effect of baking under a high mechanical pressure was investigated. Since an increased internal pressure could have a beneficial effect on the binder coke yield this aspect has also been examined, viz., by baking under pneumatic pressures up to 500 psig and a variety of heating rates.

#### 1. Mechanical Pressure Baking

Experiments were conducted with Kish-binder, and petroleum coke-Thermax-binder systems.

##### Kish-Binder

This system was chosen because of the highly ordered nature of the graphite crystallites in the Kish, thus establishing a high carbon structure density. The results have been summarized in Table IV. Since Kish contains about 23% ash, most of which is lost during graphitization, the graphitized densities have been recalculated with the assumption that the Kish was pure. A comparison with specimen AC5-2, the blank, shows a considerably favorable effect of baking Kish-binder systems under mechanical pressure.

TABLE VI  
Effects of Baking Under Pressure

Pressure psig	Time hrs.	Final Temp. °C	Carbon Residue from Binder %	Volume Changes in Baking %	A D After Baking
80	8	540	72.5	+ 1.6	1.66
200	8	540	73.9	+ 2.4	1.65
500	8	540	75.7	+ 3.0	1.65
80	64	540	77.9	- 1.7	1.72
250	64	540	78.0	- 1.5	1.72
80	8	540	72.5	+ 1.6	1.66
80	16	540	78.3	+ 0.7	1.68
80	32	540	78.4	- 1.1	1.71
80	64	540	77.9	- 1.7	1.72
80	96	540	76.4	- 2.8	1.73
0	96	540	63.1	- 2.5	1.69

### Calcined Coke-Thermax-Binder

The data of Table V show conclusively that mechanical pressure baking had no beneficial effect at all on the final densities of the specimens of this three-component system.

TABLE V  
Mechanical Pressure Baking

	<u>Parts Thermax/100 Parts Coke</u>					
	<u>0</u>		<u>15</u>		<u>25</u>	
	<u>Baked</u> <u>A D</u>	<u>Graph.</u> <u>A D</u>	<u>Baked</u> <u>A D</u>	<u>Graph.</u> <u>A D</u>	<u>Baked</u> <u>A D</u>	<u>Graph.</u> <u>A D</u>
Mechanical	1.56	1.55	1.68	1.68	1.70	1.71
Conventional	1.57	1.58	1.68	1.70	1.73	1.79

### 2. Pneumatic Pressure Baking

There are two aspects to the effect of baking under pneumatic pressure on the maximization of the overall process of making high density graphite. They are the effect on the carbon residue of the binder and the effect on the impregnability of the resulting baked carbon with pitch.

### Effect on Binder Coke Yield and Volumetric Shrinkage

Table VI shows the data obtained when molded specimens containing 65 parts coke flour, 35 parts Thermax and 29 parts coal tar pitch binder were baked under various pressures and with various heating cycles. The following can be concluded. The pressure increases the binder coke yield considerably.

The effect increases as the heating cycle is increased from eight hours to sixteen hours but remains virtually constant beyond this time.<sup>1</sup> During the short heating cycles an expansion of the piece takes place which may be associated with the fact that the solidification temperature for the specimen increases with increasing pressure, causing a greater thermal expansion. Thus, the density of a baked specimen increases with increasing baking cycle time. However, no benefit is derived from baking under pressures greater than 80 psig and this value, together with a baking cycle of 96 hours (25° - 540° C) was adopted for subsequent experimentation.

The increase in the binder coke residue caused by baking under pressure was also apparent from the results of an experiment which was designed for a more thorough evaluation of pressure baking. The design is shown in Figure 9 and the results in Figure 10. Figures 11 and 12 are graphical representations of the binder coke residue and the volumetric shrinkage during baking under atmospheric and under elevated pressures as functions of the Thermax content of the mix.

It can be seen that the effect of pressure baking is to increase the binder coke residue in all mixes containing Thermax, and to bring the residues to the same level irrespective of the Thermax content. The effect on the all-flour mix is small, however. On the other hand, pressure reduces the volumetric shrinkage with all mixes, so that the net effect on the apparent densities is zero for the all-flour mix and small, of the order of 2%, on the Thermax mixes.

1. No explanation can be offered for the small decrease as the heating cycle is increased further to 96 hours.

### Effect on the Impregnability of Resulting Baked Carbon

The experimental design of Figure 9 also allows the evaluation of the effect of pressure baking on the impregnability of the resulting baked carbon. A comparison between the data of Groups 1 and 4 and of Groups 2 and 3 in Step 3 (Figure 9) shows that the specimens baked at atmospheric pressure are more amenable to impregnation than those baked at a higher pressure, the weight gains of the pressure baked specimens being considerably lower than the weight gains of the specimens baked under atmospheric pressure.

The effect of rebaking impregnated specimens can be seen by comparing the results from Group 1, Steps 3A and 4, with those from Group 4, Step 4. (Figure 9). It is clear that baking under pressure increases the density, since the increase in the carbon residue of the impregnant is not, in this case, offset by a decrease in the volumetric shrinkage.<sup>1</sup>

The results can be summarized as follows:

On the three-component systems the benefits derived from pressure baking decrease as the Thermax content is increased. The impregnability is reduced by baking under pressure in the previous processing step, but pressure baking of impregnated specimens increases their densities.

1. The low carbon residues can be ascribed first to the higher baking temperature so that any weight loss by the specimen exclusive of that due to the specimen is attributed to the impregnant, and secondly, to mechanical losses.

#### A 4 Impregnation

For the discussion of this processing step, reference is made again to Figures 9 and 10. The first impregnation was carried out with Koppers' pitch oil, filtered and topped. (See Step 3). The data show that the degree of impregnation is some inverse function of the concentration of Thermax in the mix. This can be explained by the smaller pore size of the specimens caused by the Thermax preventing the pitch from completely penetrating all pores.

The second impregnation (Step 5) was carried out with Resin C, a single phase coal tar derivative which has a lower average molecular weight and size than Koppers' pitch oil. In general, the degree of impregnation with Resin C was somewhat greater than with the impregnant from pitch oil. As experienced before, however, the degree of impregnation decreased with increasing Thermax content in the three-component systems.

#### A 5 Graphitization

It is essential for the attainment of high densities that the volumetric shrinkage during graphitization be as large as possible. Since the manner in which carbon is processed before graphitization is an important factor in determining the eventual shrinkage, the effect of this factor was evaluated by graphitizing the specimens used in the previously discussed investigations to 2900° C at an upheal rate of 0.5° to 1.0° C per minute.

Considerable shrinkage of the specimens occurred with the mixes containing Thermax, the shrinkage being largest for the specimens formulated with 35 parts Thermax. From a comparison of the data from Steps 1 and 4 with those from Steps 2 and 3, it is apparent that the shrinkage during graphitization of specimens formulated with Thermax is larger when originally baked under atmospheric than under a higher pressure, whereas the shrinkage of the all-flour (XXIX) mix appears to be independent of the type of baking. Only the specimens formulated with 35 parts Thermax reached a density of 1.90 or better and they experienced a gain in density of about 2 to 4% during graphitization.

#### B. Extruded Stock

Since a more effective alignment of the geometrically anisotropic coke particles resulting in a larger shrinkage of the carbon during graphitization could be expected as a result of extrusion as compared to molding, a study was made of the processing of extruded specimens 2" in diameter.

##### B 1 Formulation

During the work with molded specimens, it was determined that the highest densities in the three-component system were reached with a 65/35 coke flour/Thermax ratio. This ratio was adopted for experiments with extruded stock. The binder level had to be determined separately, however. This was done by extruding a number of mixes with varying parts of binder. The advisability of adding polyvinyl chloride to the binder as a coke residue promotor was investigated concurrently.

For the same reasons presented in the section on molded stock, all-flour mixes were processed simultaneously with the three-component mixes. The results are summarized in Table VII.

TABLE VII

Density Characteristics of Extruded Stock

Mix Number	Coke (Parts)	Thermax (Parts)	Binder (Parts per 100 parts aggregate)	Apparent Density	
				Green	Baked
XV A*E 29	65	35	29	1.77	1.75
XV A E 31	65	35	31	1.75	1.75
XV E 31	65	35	31	1.76	1.75
XV E 33	65	35	33	1.74	1.68
XV A E 33	65	35	33	1.73	1.74
XXIX A E 27.5	100	-	27.5	1.60	1.57
XXIX A E 30	100	-	30	1.53	1.51
XXIX A E 33	100	-	33	1.60	1.59
XXIX A E 36	100	-	36	1.61	1.56
XXIX E 36	100	-	36	1.64	1.62
XXIX A E 39	100	-	39	1.56	1.53

\* The letter A denotes 0.5% polyvinyl chloride added to the mix.

It can be concluded from these data:

- (a) That the mixes containing Thermax have higher densities in the baked state than the all-flour mixes.
- (b) That the addition of 0.5% polyvinyl chloride to the mix provides no improvement in density.



- (c) That the optimum binder content for the three-component mix is approximately 31 parts binder per 100 parts aggregate and for the all-flour mix approximately 36 parts binder per 100 parts aggregate.

Further experiments were carried out with mixes of the above compositions, the three-component mix having been given the designation XV E 31 and the two-component mix XXIX E 36.

The coke used for the formulation of the above mixes was petroleum coke I. (See Section VI A 1) This coke was also used in the determination of the effect of multiple impregnations of baked stock on the graphitized density, for some experiments on impregnation of graphitized stock and on gaseous deposition.

After the principal steps of the process were determined another lot was extruded with coke II. This lot received the designation XV E B 31.

#### B 2 Baking

The extruded pieces from the XV E 31 and XXIX E 36 mixes were baked in an essentially gradient free furnace under atmospheric pressure at a rate of 5° C per hour. This furnace provided two-sided heating. After baking many of the pieces were found to be cracked. These cracks did not appear when the pieces of the XV E B 31 mix were subsequently baked at the same upheat rate in a different furnace which provided essentially one-sided heating.

### B 3 Impregnation

Figures 13 and 14 are flow diagrams of the processing of the XV E 31 and XXIX E 36 mixes, respectively.

The impregnations were carried out with Koppers' filtered and topped pitch oil. In accordance with the conclusions from the processing of the mold stock (Section A 3), the rebake after the first pitch impregnation was carried out at atmospheric pressure. Rebakes after any further impregnations were done under 80 psig pressure to 540° C and at atmospheric pressure between 540° and 850° C. In one bake involving two specimens, the packing was omitted in the hope that without packing no impregnant would be absorbed by the packing material and the coke yield would be higher. The results were not conclusive, however. (See Figure 13)

The following conclusions can be drawn from Figure 13 (three-component mix).

1. The reproducibility of the impregnation process is very good. This is clear from a comparison of the various specimens at the same stage of processing.
2. Little is gained in the baked state by a third impregnation, and a fourth impregnation is virtually without effect.
3. The highest graphitized densities were obtained with specimens which had been impregnated once and twice in the baked state. Further impregnations appear to have a detrimental effect on the final densities.

4. The shrinkage (gain in density) during graphitization is highest with only one impregnation in the baked state. The smaller shrinkage after two impregnations offsets the gain in density made in the second impregnation.

This law of diminishing returns was also operative when the graphitized specimens were impregnated. (Figure 13).

1. The largest increase in density was obtained with the specimen which had never been impregnated before, whereas the density increase was almost insignificant with specimens which had been subjected to three or four impregnations in the baked state.

2. Two impregnations after graphitization of unimpregnated baked stock had almost the same effect as one impregnation in the baked state followed by one in the graphitized state.

On the basis of these results, the processing of batch XV E B 31 was carried out with only one impregnation in the baked state followed by atmospheric baking. It is apparent from Figure 15 that this procedure is indeed very effective since the increase in density during graphitization was even more than experienced with the previous lot, viz. 0.13 - 0.16 g/cc as compared to 0.12 - 0.14 g/cc. Impregnating this graphitized stock once or twice and regraphitizing yielded a set of eight specimens ranging in density from 1.94 to 2.01, but with more than half having a density of 1.98 and above.

After the first bake, specimens 10, 12 and 15 were impregnated with 15 Vacuum pitch. The weight gains were only 1 to 2% as compared to ca 5 to 7% with Resin C. This type of pitch

(for its properties, see Section VI C) is apparently unsuitable for the impregnation of materials like those discussed here.

TABLE VIII

Impregnation of Baked Extruded Stock with Resin C and 15 Vacuum Pitch

Resin C				15 Vacuum Pitch			
Specimen	Apparent Density Before Impregnation	Density After Impregnation	$\Delta A D$ %	Specimen	Apparent Density Before Impregnation	Density After Impregnation	$\Delta A D$ %
XV E B 31-1	1.76	1.86	6.8	10	1.76	1.79	1.7
-4	1.77	1.85	4.5	12	1.75	1.78	1.7
-13	1.77	1.86	5.1	15	1.77	1.79	1.1

The substitution of topped Resin C for filtered and topped Koppers' pitch oil has no effect on the impregnating efficiency. This is an important point in that the availability or non-availability of various impregnating agents may necessitate substitution of another pitch of similar properties as Resin C and Koppers pitch oil without such substitution resulting in any particular processing difficulties.

Figure 14 refers to the processing of the two-component all-ooke flour mix. Two different paths were followed, one involving four impregnations before graphitization and one involving two impregnations before and two after graphitization. The latter path appears to give somewhat better results. Here again, exhaustive impregnation before the first graphitization appears to be counter-indicated and may even be harmful.

In both instances, however, the densities remained considerably below those obtained with the three-component mixes.

#### B 4 Graphitization

(a) Specimens 5 and 6 (Figure 13) were graphitized at a relatively fast rate of 1.5 to 2.0° C per minute. All other specimens were graphitized at a rate of 0.5 to 1.0° C per minute. This difference in heating rates explains the fact that the density increase during graphitization for Specimens 5 and 6 is small compared to that of other specimens. It is important that the graphitization rate be kept low so that the maximum shrinkage can be achieved. For the graphitization of the specimens in the XV E B 31 series, the following schedule was therefore adopted:

Room temperature - 700° C	200° C per hour
700° C - 1300° C	60° C per hour
1300° C - 2100° C	30° C per hour
2100° C - 2500° C	60° C per hour
2500° C - 2900° C	Full power

(b) A comparison of the data for the three-component mix with those of the two-component mix (Figures 13 to 15) shows that the increase in density during graphitization is much larger for the mixes containing Thermax than for the all-flour mix. This confirms the observations made with molded stock (Section VII A 5) Whereas densities in excess of 1.90 and approaching 1.95 are easily obtained with the three component mixes, the highest density obtained with an all-flour mix was 1.84. Since there was no indication that the latter value could be increased, no further work was done with the all-flour mix.

(c) The specimens of the XV E B 31 series all have a higher density level throughout the various processing stages than the specimens of the XV E 31 series. This must be attributed to the different petroleum coke used, although the change to a different type baking furnace may also have contributed to some extent. It is also interesting to note that in the XV E B 31 series the last six specimens had a slightly higher green density than the remaining specimens. This must be attributed to the combined effects of variations in mixing and extrusion. The individual differences in density are partly eliminated, however, during further processing.

#### B 5 Purification

Three impregnated and baked specimens and one specimen which had been impregnated, graphitized, reimpregnated, and rebaked were graphitized to 2500° C in the purification unit, according to the F process.<sup>1</sup> This modified procedure did not appear to have any effect on the densities of the finished pieces. An ash determination was made on one of the specimens (XV E B 31-12) and the result compared with the ash content of specimen XV E B 31-2, which had not been subjected to the F process, and also with the ash of purified Superflake 198 graphite. The results are summarized in Table IX.

1. Contract No. AT(11-1)-172. Final Report by L. H. Juel.

TABLE IX

Efficiency of the F Process with High Density  
Synthetic and Superflake Graphite

<u>Material</u>	<u>Ash (ppm) *</u>
Extruded - XV E B 31 - 12 - Purified	72 $\pm$ 2**
Extruded - XV E B 31 - 2 - Not purified	100
Superflake 198 - Purified	6
Superflake 198 - Not purified	8100

\* 1697° F

\*\* Average of two determinations

It is clear that the F process in its present form is unsuitable for the purification of high density graphite as prepared in a manner discussed in this report. The reason for this must be sought in the distribution and the nature of the porosity which is such as to prevent adequate diffusion of the purifying gases towards the center of the piece and of the fluorinated ash constituents out of the piece.

B 6 Gaseous Deposition

In order to reach the porosity of exhaustively impregnated graphitized specimens inaccessible to liquid pitch-like hydrocarbons, further densification experiments were made in which carbon was deposited in the pores of the graphite by means of pyrolytic decomposition of gaseous hydrocarbons. Specimen temperatures consistent with the deepest penetration of the gas before decomposition and with the most favorable rate of carbon pickup were explored first. These experiments were mainly made with briquetted and molded specimens.

Table X shows the results of gaseous deposition obtained with propane and with methane on a number of specimens having a wide range of densities.

TABLE X

Densification by Deposition of Carbon Through the Pyrolysis of a Hydrocarbon Gas

Sample Description	Gas <sup>1</sup>	Total Time(hrs.)	Temp. °C	Density g/cc		$\Delta$ A D
				Before	After	
XXIII-1 <sup>2</sup>	Propane	176	700	1.75 <sub>4</sub>	1.94 <sub>1</sub>	0.18 <sub>7</sub>
XXIII-2	Methane	102	900	1.76 <sub>0</sub>	1.90 <sub>5</sub>	0.14 <sub>5</sub>
XV-5 <sup>2</sup>	Propane	136	700	1.91 <sub>8</sub>	1.93 <sub>0</sub>	0.01 <sub>2</sub>
XV-6	Propane	184	700	1.94 <sub>8</sub>	1.97 <sub>2</sub>	0.02 <sub>4</sub>
AC9-7 <sup>3</sup>	Propane	112	700	2.00 <sub>1</sub>	2.03 <sub>4</sub>	0.03 <sub>3</sub>
AC9-2 <sup>4</sup>	Propane	156	700	1.84 <sub>6</sub>	1.96 <sub>4</sub>	0.11 <sub>8</sub>
M-2 <sup>5</sup>	Methane	61	1000	1.70 <sub>6</sub>	1.80 <sub>4</sub>	0.09 <sub>8</sub>
M-3	Methane	109	950	1.71 <sub>2</sub>	1.79 <sub>2</sub>	0.08 <sub>2</sub>
M-6	Methane	210	900	1.68 <sub>7</sub>	1.86 <sub>1</sub>	0.17 <sub>4</sub>

1. Flow rates: 12 liters/hr. for Propane  
14 liters/hr. for Methane

2. Mixes XXIII and XV: 65 parts coke flour, 35 parts Thermax,  
29 parts pitch binder.

3. Flake graphite - Fura-Tone briquette (cf Section C 1 b)

4. Flake graphite - polyvinyl chloride briquette (cf Section C 1 b)

5. M denotes Great Lakes Carbon mold stock



TABLE XI

Gaseous Deposition Data on High Density Extruded Graphite

Specimen	Number of Impregnations		Duration of Run (hrs.)	A D (g/cc)		Initial Rate $\frac{\Delta W}{W \Delta t} \times 10^{-4}$
	Before Graph.	After Graph.		Before	After	
XV E 31-1	0	0	113	1.84	1.90	5.4
XV E 31-2	0	2	160	1.93	1.96	1.9
XV E 31-8	1	1	190	1.93	1.95	0.5
XV E 31-5	3	0	39	1.85	1.85	0.6
XV E 31-7	4	1	66	1.92	1.92	0

Carbon pickup occurred in all instances. The influence of time is shown in Figure 16. The specimens with a density of 1.84 and below all experienced an initial density increase at the same rate. However, the remaining three specimens which had a density of 1.92 and above gained at a much slower rate.

In the few experiments that were done, no significant differences were found between the results with propane and with methane. Because of the lower temperature required with propane (695° to 705° C) as compared to methane (ca 900° C), the densification experiments with extruded stock were carried out with propane. The results are incorporated in Figures 14 and 15.

It is apparent that the largest density increases were obtained with specimens, XV E 31-1 and XV E B 31-3, which had never been pitch impregnated at any time.\* The greater the number of impregnations performed on the specimens, the smaller the rate and magnitude of increase in density. This can also be seen from Table XI in which the rates of increase in density are summarized. A smaller pore size and pore volume decrease the rate of the deposition reaction to the point that it becomes far too slow to be practical. This is particularly apparent with specimens XV EB 31-1 and - 6 which experienced only a minor weight gain in the first twenty-four hours, but did increase in weight when subjected subsequently to pitch impregnation.

It is apparent that little is gained by using the gaseous deposition technique when all other phases of the conventional process are maximized.

\* Specimen XV AE 29-5 was a run made to check the conditions established previously with briquettes.

## B 7 Properties of High Density Extruded Stock

Apparent density and elastic modulus were measured in a non-destructive manner on all specimens. Crushing strength, cross-breaking strength, coefficient of thermal expansion, and electrical resistivity were measured on specimen XV E B 31-9, which was sectioned for the purpose. The ash content was determined on specimen XV E B 31-2. The results tabulated in Table XII are, therefore, typical rather than average.

TABLE XII  
Properties of High Density Graphite

Apparent Density, g/cc	1.95 - 2.01	
Elastic Modulus, psi x 10 <sup>6</sup>	2.8 - 3.3	
Crushing strength, psi    Transverse	3400 ± 1400	1
Axial	8800 ± 700	2
Cross Breaking Strength, psi, Transverse	(1300)	3
Axial	4000 ± 500	2
Coefficient of Thermal Expansion, °C <sup>-1</sup> x 10 <sup>6</sup>		
Transverse	6.1	2
Axial	3.4	
Electrical resistivity, ohm in x 10 <sup>-4</sup>		
Transverse	10.1	1
Axial	4.25	2
Ash, %	0.01	

1. Average of three determinations.
2. Average of two determinations.
3. Specimen showed cracks before testing.

The large anisotropy of the properties is apparent, the properties in one direction having values about twice those in the other direction. This is undoubtedly due to a high degree of alignment of the anisotropic particles during extrusion.

TABLE XIII

## ELASTIC MODULUS DATA FOR HIGH DENSITY GRAPHITE

Spec. No.	Green		Baked		Impregnated and Baked		Graphitized		Purified		Reimpregnated Baked and Graph		Reimpregnated Baked & Purified		Reimpregnated Baked & Graph	
	AD	E <sup>1</sup>	AD	E	AD	E	AD	E	AD	E	AD	E	AD	E	AD	E
XV EB-1	1.72	2.72	1.76	3.65	1.81	4.20	1.94	2.85	---	---	1.98	n.m. <sup>3</sup>	---	---	2.01	3.01
-2	1.72	2.76	1.73	3.39	1.80	4.41	1.94	2.94	---	---	---	---	---	---	---	---
-3	1.72	2.48	1.74	3.43	---	---	1.86	n.m.	---	---	---	---	---	---	---	---
-4	1.73	2.90	1.77	3.65	1.82	4.28	1.95	2.96	---	---	---	---	1.96	---	---	---
-5	1.72	2.74	1.73	3.45	---	---	1.86	n.m.	---	---	---	---	---	3.03	---	---
-6	1.72	2.84	1.74	3.68	1.79	4.25	1.92	2.93	---	---	1.95	n.m.	---	---	1.97	3.10
-7	1.71	2.60	1.75	3.27	1.79	4.10	1.92	2.61	---	---	1.94	2.74	---	---	---	---
-8	1.67	2.45	---	---	---	---	---	---	---	---	---	---	---	---	---	---
-9	1.72	2.55	1.75	3.05	1.81	3.94	1.95	2.71	---	---	1.98	2.88	---	---	---	---
-10	1.73	2.76	1.76	3.45	1.82	n.m.	---	---	1.96	2.82	---	---	---	---	---	---
-11	1.73	2.65	1.74	3.39	1.79	n.m.	1.94	2.90	---	---	1.95	2.88	---	---	---	---
-12	1.72	2.62	1.75	3.29	1.80	n.m.	---	---	1.94	n.m.	---	---	---	---	---	---
-13	1.75	2.86	1.77	3.38	1.81	4.11	1.96	3.06	---	---	---	---	---	---	---	---
-14	1.71	2.42	---	---	---	---	---	---	---	---	---	---	---	---	---	---
-15	1.74	2.81	1.77	3.69	1.82	n.m.	---	---	1.95	2.97	---	---	---	---	---	---
-16	1.73	2.65	1.77	3.53	1.83	n.m.	1.97	3.10	---	---	1.99	3.00	---	---	---	---
-17	1.75	2.66	1.78	3.90	1.82	4.78	1.96	3.16	---	---	2.00	3.28	---	---	---	---
-18	1.75	2.92	1.76	3.69	1.82	---	1.98	3.20	---	---	1.98	3.20	---	---	---	---

1 E in psi x 10<sup>6</sup>

2 --- means: process step not carried out

3 n.m.: not measured

The structure of the graphite was not free from flaws. Internal cracks were present, most of which were shrinkage cracks formed during baking and/or graphitization. Some flaws, however, had their origin in the extrusion process, and could have been boundary surfaces between successive batches of the same mix. These surfaces were created during successive recharging of the extruder mud chamber. All these flaws have contributed significantly to limiting the highest density attained to 2.01. It must be concluded, therefore, that even higher densities can be reached if these flaws can be eliminated by modifying the method of re-extrusion employed and the baking procedure.

In order to determine the radial density distribution specimen XV E B 31-11 was turned down on a lathe in steps of .06 to .08 inches, and the density of the remaining piece measured. This density is plotted against the radius in Figure 17. It can be seen that the density decreases rather sharply towards the inside of the piece. Since the occupation of the pores by the impregnant decreases towards the center, it is important that the initial steps in the process are maximized to their full extent.

The elastic modulus was measured during processing in order to determine the effect of the various steps upon this property. The data are summarized in Table XIII. In Figure 18 the average values of E at each density are plotted against the density. In all instances there is a correlation between the elastic modulus and the density. It is interesting to note that impregnating and rebaking of baked stock does not affect the correlation for the baked stock. This suggests that the impregnant coke is strongly bonded to the original

specimen carbon. This is not quite true in the graphitized state, where the modulus of graphitized, reimpregnated and regraphitized stock is lower than that of graphitized stock of the same density. In this case the impregnant carbon probably remains more or less independent from the main body of graphite.

In other respects the modulus behaves according to expectations. The green stock, with its pitch matrix, has the lowest modulus. A considerable increase occurs in baking, during which a very hard carbon is formed. During graphitization the material becomes softer again, to yield a final modulus of about  $3.1 \times 10^6$  psi for the highest density material.

#### C. Natural Graphite Briquettes

Natural graphite was chosen as a candidate component of high density graphite because the almost perfect orientation of the crystallites in the flakes would result in a higher initial carbon structure density. However, the work with Kish has shown that such a system could not be firmly bonded with regular coal tar pitch binders, for specimens so bonded had a tendency to exfoliate or intumesce upon graphitization. It was, therefore, thought that polymeric binders, preferably of the three-dimensional thermosetting type, would be more suitable for use in flake graphite systems. When such a flake graphite-binder mixture is polymerized under pressure, the carbon structure is frozen in at its maximum density. A higher density product might thus be expected to result.

## C 1 Formulation

### (a) Graphite

In order to choose a graphite yielding the highest carbon structure density, the compressed densities of a number of binder-free materials were determined. The results are shown in Table XIV. Although experiments with Superflake 198, purified, were not initiated until later, this material is incorporated in the table for convenience. Superflake 192 showed the highest relaxed density, followed by Superflake 198, purified and unpurified. Superflake 198 was chosen for use in further experiments because of its lower ash content.

TABLE XIV

Compressed Density of Binder-free Finely Divided Graphite\*

Material	Density	
	Compressed**	Relaxed
Kish	1.92	---
Superflake No. 192	2.16	2.00
Superflake No. 198	2.030	1.925
Superflake No. 198, purified	2.090	1.955
Petroleum Coke Flour (Calcined)	1.59	---
Petroleum Coke Flour (Graphitized)	2.00	1.68

\* Compressed bodies of 2" diameter x ca 1".

\*\*All studies made at 6000 psi.

### (b) Binder

The following materials were considered as possible

binders:

Polyvinyl chloride,  
Polystyrene,  
A phenolic resin of German manufacture,  
Fura-Tone 1347, a furfural-acetone polymer manufactured  
by Irvington Varnish Company.

Sound briquettes were obtained with polystyrene and with Fura-Tone as binders. Since the latter yielded briquettes of density 2.00 as compared to 1.96 for the briquettes formulated with polystyrene, Fura-Tone was considered the more suitable binder. In order to obtain more complete mixing with the graphite, the resin was employed as a 20% solution in benzene or alcohol, the solvent evaporating during processing.

It was found that sound briquettes could be made either with or without an accelerator (p-toluene sulfonic acid) added to the resin. More consistent results and higher densities were obtained, without the accelerator.

#### C 2 Forming

The briquettes formulated with a binder were molded either in a regular mold or in a split mold at a pressure of 5000 psi. A few specimens were formed at 4000 psi. The molding temperatures ranged from 250° to 540° C for the specimens prepared with a binder. At the lower temperatures the binder was just allowed to set; at 540° C the binder was carbonized.

The binder-free briquettes were molded at 6000 psi and kept at room temperature during pressing. Whereas the binder-free briquettes could easily be ejected from the mold without lamination taking place, considerable difficulties were encountered during ejection of the briquettes which had been formulated with a binder. It was found that the only sound specimens were obtained when ejected hot. The reason for this must be found in the much larger coefficient of thermal expansion of the mold material compared to that of the graphite. During molding at elevated temperatures the specimens will conform to the mold. Upon cooling, however,



TABLE XV

Densities of Flake Graphite Briquettes

Sample	Mold	Graphite	% Binder	Molding Pressure psi	Molding Temperature °C	A D g/cc
AC9-21	Reg.	Superflake 198	10	5000	540	1.942
AC9-22	"	Superflake 198	10	5000	540	1.964
AC9-23	"	Superflake 198	10	5000	540	2.018
AC9-24	"	Superflake 198	10	5000	300	1.999
AC9-25	"	Purified Superflake	--	6000	25	1.848
AC9-27	"	Purified Superflake	10	5000	325	1.893
AC9-28	"	Purified Superflake	10	5000	540	1.896
AC9-30	Split	Purified Superflake	10	4000	270	1.983
AC9-32	"	Purified Superflake	10	4000	280	1.934
AC9-33	"	Purified Superflake	10	4000	< 90	1.975
AC9-34	"	Purified Superflake	10	4000	255	1.930
AC9-37	Reg.	Purified Superflake	--	6000	25	1.828
AC9-39	"	Purified Superflake	--	6000	25	1.855
AC9-50	"	Purified Superflake	--	6000	25	1.838
AC9-51	"	Purified Superflake	--	6000	25	1.833

the mold will contract more than the specimen. It is believed that the non-uniform release of the resulting radial stresses is the major cause of the lamination cracks formed during ejection.

Hot ejection yielded satisfactory specimens of mixes prepared from the "as received" Superflake 198. After this graphite was purified by heating to 2900° C no sound specimens could be obtained.

Since the non-uniform stress release during ejection was still thought to be at the root of the difficulties, a split mold was used for briquetting the purified graphite-Fura-Tone mix. However, some of the mix was pressed into the crevices of the mold assembly; as a result, the mold stuck to the containing block and unsuitably large pressures were required for ejection. Nevertheless, a number of sound briquettes were obtained. It is believed that a different mold design could have prevented the sticking of the mold.

Table XV shows some typical results. It can be seen that although some high densities were obtained, the reproducibility of the densities of the briquettes containing Fura-Tone is only fair. The binder-free briquettes show a very good reproducibility. The densities attained with the "as received" Superflake appear to be higher than those attained with the purified graphite. As was to be expected, the binder-free briquettes have the lowest densities.

### C 3 Densification

In order to raise the densities of the briquettes to the desired value of 2.00 g/cc or more and at the same time to increase the bonding between the constituent particles, the specimens were subjected to the pyrolytic decomposition of

hydrocarbon gases inside the pores. Propane was generally used at a temperature of 700° C, although methane at 900° C was also employed in one or two instances. The principal advantage of propane over methane is the lower decomposition temperature of the former. It was found that the smaller molecular size of methane did not offer any particular advantages to warrant operation at the higher temperature.

The results of the densification runs are presented in Table XVI. A few specimens which had been formulated with Fura-Tone reached a density of 2.00. The most consistent results were obtained with the binder-free specimens, however, nearly all of which could be densified to 2.00 density or above. These specimens appear to be well bonded, and it may be concluded that the use of a binder during molding is not required.

TABLE XVI

Densification of Pressed Flake Graphite Briquettes by Gaseous Deposition

Sample	Graphite	Binder %	Duration of Run (hrs.)	Apparent Density g/cc	
				Before	After
AC9-22	Superflake 198	10		1.964	1.983
AC9-23	"	10		2.018	2.032
AC9-28	Purified Superflake	10	215	1.896	1.940
AC9-30	"	10	122	1.983	1.987
AC9-33	"	10	109	1.975	2.006
AC9-37	"	-	180	1.828	1.963
AC9-38	"	-	220	1.848	1.979
AC9-39	"	-	442	1.855	2.046
AC9-48	"	-	182	1.834	2.016
AC9-49	"	-	217	1.834	2.019
AC9-50	"	-	187	1.838	2.002
AC9-51	"	-	187	1.833	2.017

This method of preparing high density graphite is not restricted to the small specimens (2" dia. x 1") used in the above experiments, as was shown by an experiment in which a batch of Superflake 198 graphite was purified according to the F process (ash: 6 ppm) and pressed at 6000 psi in a 4" x 4" mold. The pressed plate was cut in half so as to fit in the furnace and a 4" x 2" x 2" piece was subjected to densification by deposition with propane. Its density was found to increase from 1.865 to 2.001 in about 240 hours.

#### C 4 Heat Treatment

It is a well known fact that the carbon deposited from hydrocarbon gases contains varying amounts of hydrogen. In order to remove most of this hydrogen the specimens were heated to 1600° C (upheat rate 40° C per hour). A few specimens were heated to 2000° C and to 2900° C.

In all instances an expansion occurred in addition to a weight loss, at the final temperatures. It was found, however, that usually the expansion was preceded by a shrinkage below 1200-1250° C. Figures 19 and 20 show a typical example of this behavior. The large differences in the nature of the gas carbon in the pores and the flake graphite of the main body are sufficient to cause an irreversible expansion during the upheat.

Table XVII summarizes the heat treatment data. The decrease in density of the binder-free briquettes at 1600° is insignificant and is less than that of the briquettes formulated with Fura-Tone. This confirms the conclusion of the previous section that in the systems under discussion no binder is required in order to attain high densities.

TABLE XVII

Heat Treatment of Densified Flake Graphite Briquettes

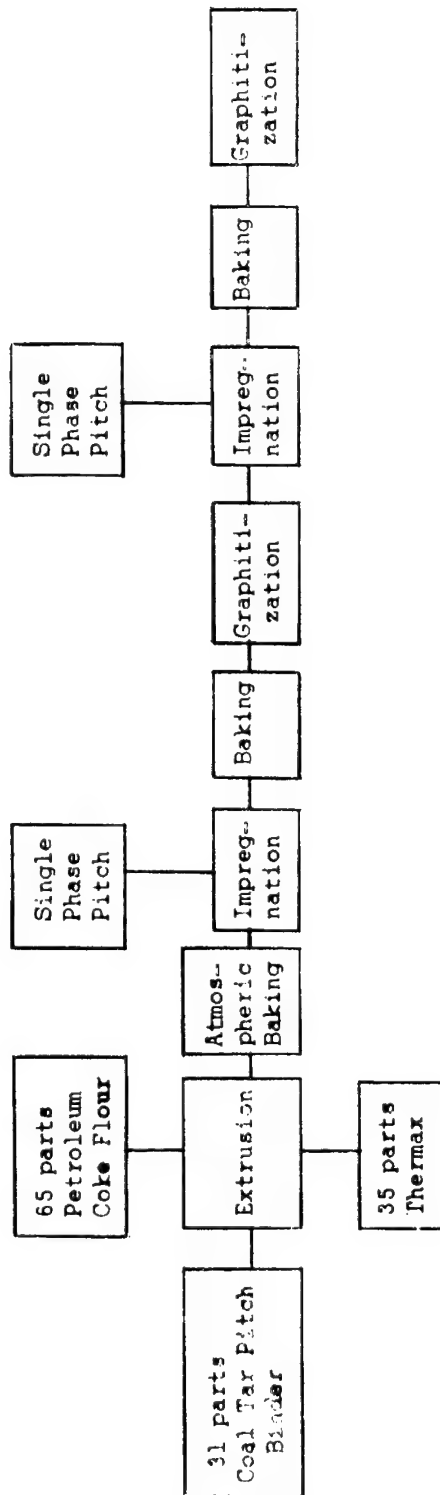
Sample	Binder %	Temperature of Heat Treat- ment ° C	Apparent Density g/cc	
			Before	After
AC9-21	10	2900	1.942	1.785
AC9-22	10	1600	1.983	1.961
AC9-22	10	2900	1.983	1.905
AC9-23	10	1600	2.032	1.996
AC9-23	10	2900	2.032	1.941
AC9-28	10	1990	1.940	1.905
AC9-33	10	1990	2.006	1.979
AC9-37	--	1990	1.963	1.952
AC9-48	--	1600	2.016	2.012
AC9-49	--	1600	2.019	2.018
AC9-50	--	1600	2.002	1.993
AC9-51	--	1600	2.017	2.015

Usually the heat treated specimens are amenable to some further densification which indicates that the expansion of the specimens is accompanied by the creation of some porosity. However, the heat treated densified binder-free briquettes had a sufficiently high density for the purpose of this work and since any further increase in density did not materially change the nature of the few briquettes subjected to a second densification procedure, it was deemed impractical to treat the remaining briquettes.

## C 5 Properties

Aside from density measurements, a crude estimate was made of the compressive strength of the densified and heat treated briquettes. The expected low shear strength made the compressive strength measurement difficult to carry out, but it can be stated that the compressive strength in the direction of molding is about 3000 psi.

FIGURE 1  
ADOPTED FLOW DIA GRAM FOR THE PRODUCTION OF HIGH DENSITY GRAPHITE



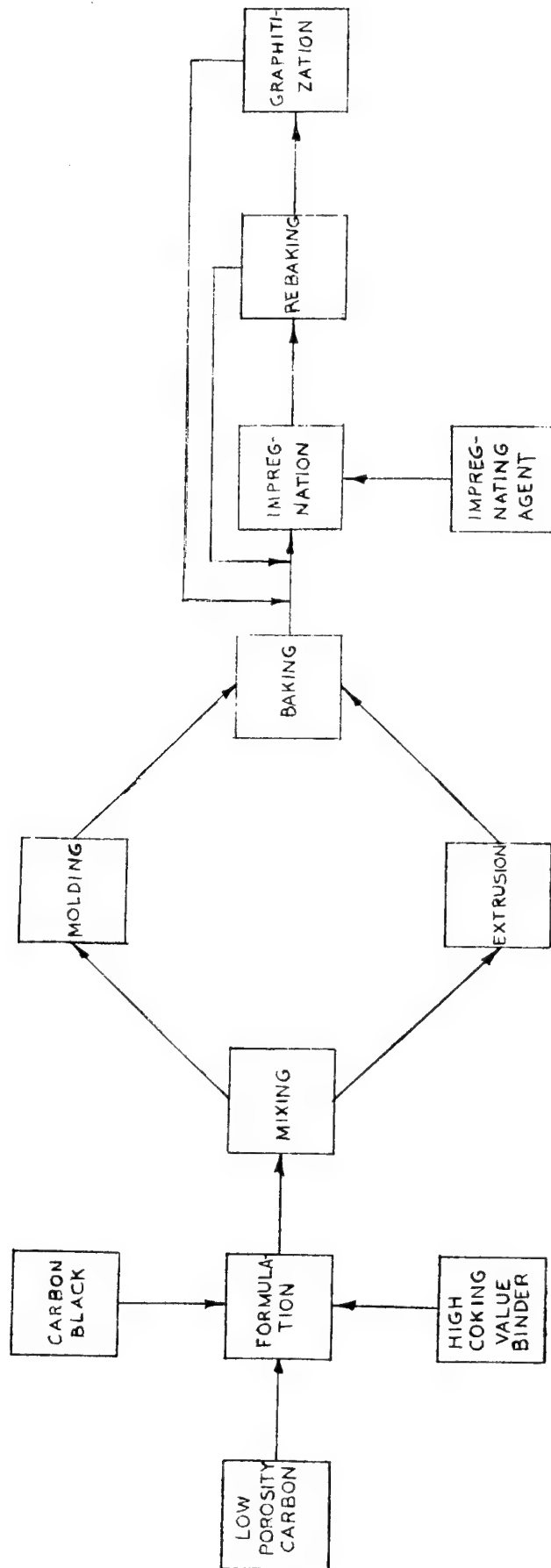


FIG. 2 -- GENERALIZED FLOW DIAGRAM FOR PRODUCTION OF HIGH DENSITY GRAPHITE.



FIGURE 3

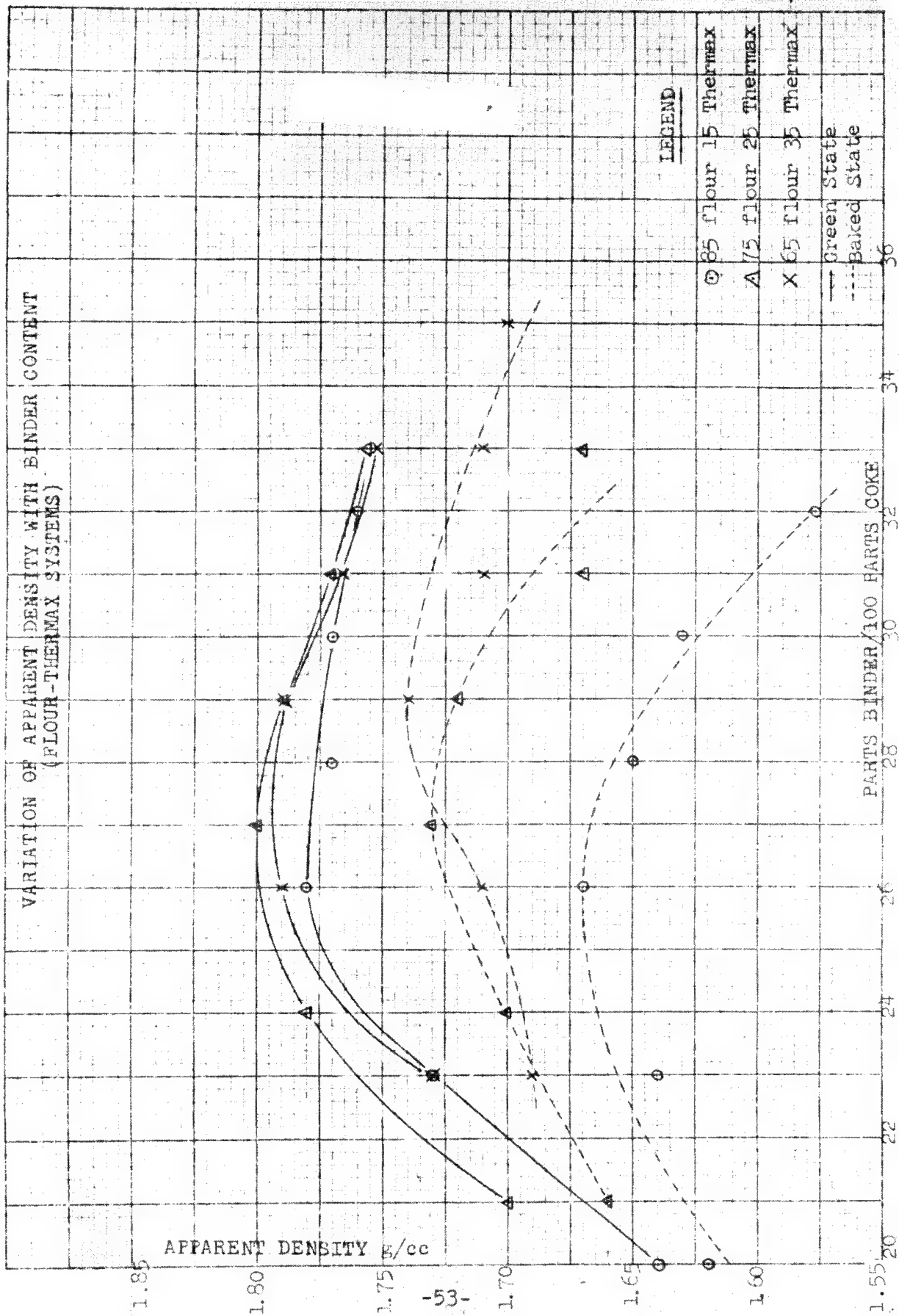


FIGURE 4

VARIATION OF APPARENT DENSITY WITH BINDER CONTENT  
(Flour-Thermax Systems)

APPARENT DENSITY g/cc

PARTS BINDER/100 PARTS COKE

1.80  
1.75  
1.70  
1.65  
1.60  
1.55

20 22 24 26 28 30 32 34 36

-54-

LEGEND

○ 85 Flour 15 Thermax

△ 75 Flour 25 Thermax

× 65 Flour 35 Thermax

— Graphite State

--- Baked State

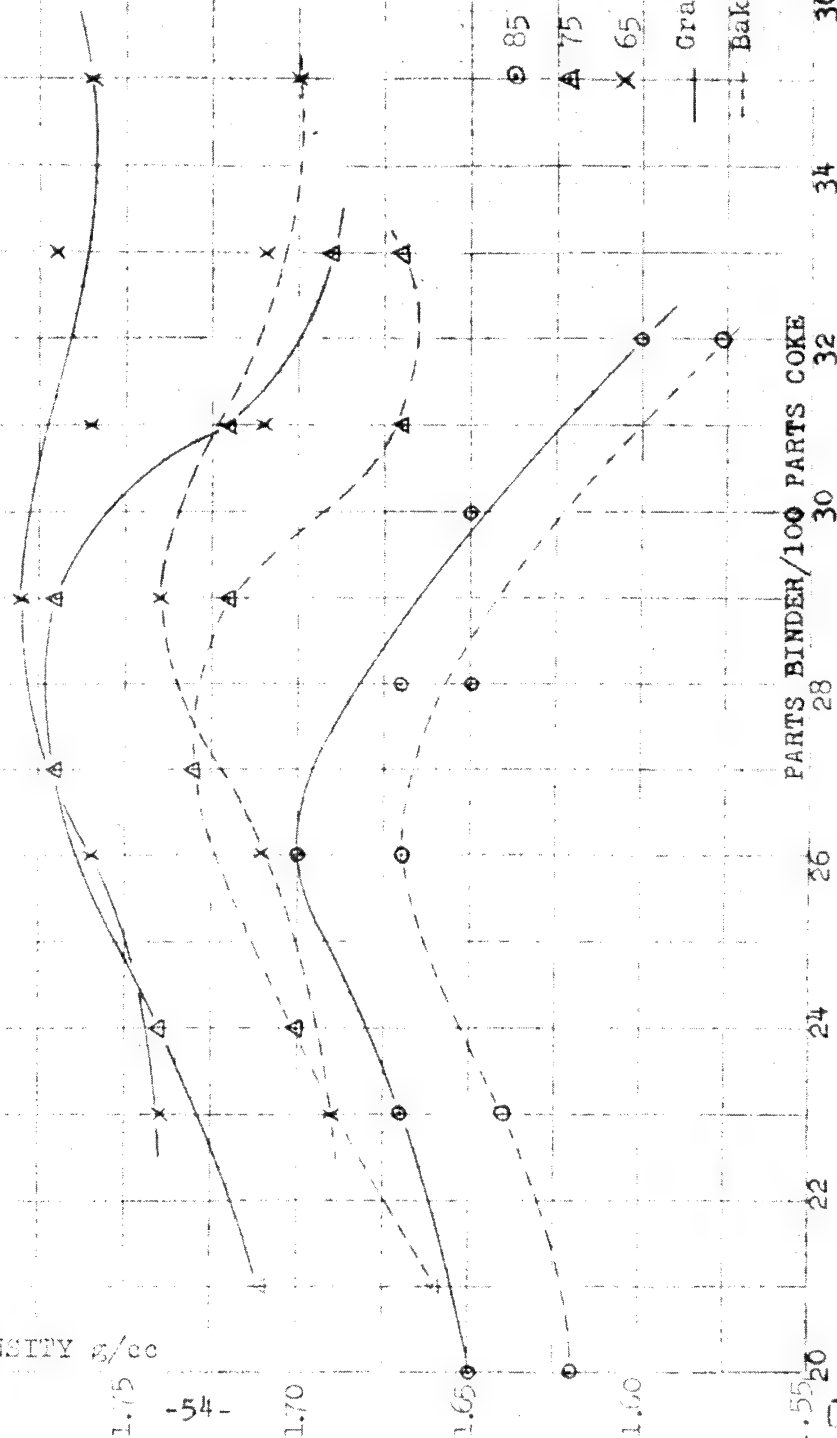


FIGURE 5

VOLUME SHRINKAGE (GREEN TO GRAPHITE STATE) VS.  
BINDER CONTENT (FLOUR-THERMAX SYSTEMS)

% Vol. Shrinkage

LEGEND

- 85 Flour 15 Thermax
- △ 75 Flour 25 Thermax
- × 65 Flour 35 Thermax

BINDER CONTENT PARTS/100 PARTS CARBON

36

34

32

30

28

26

24

22

20

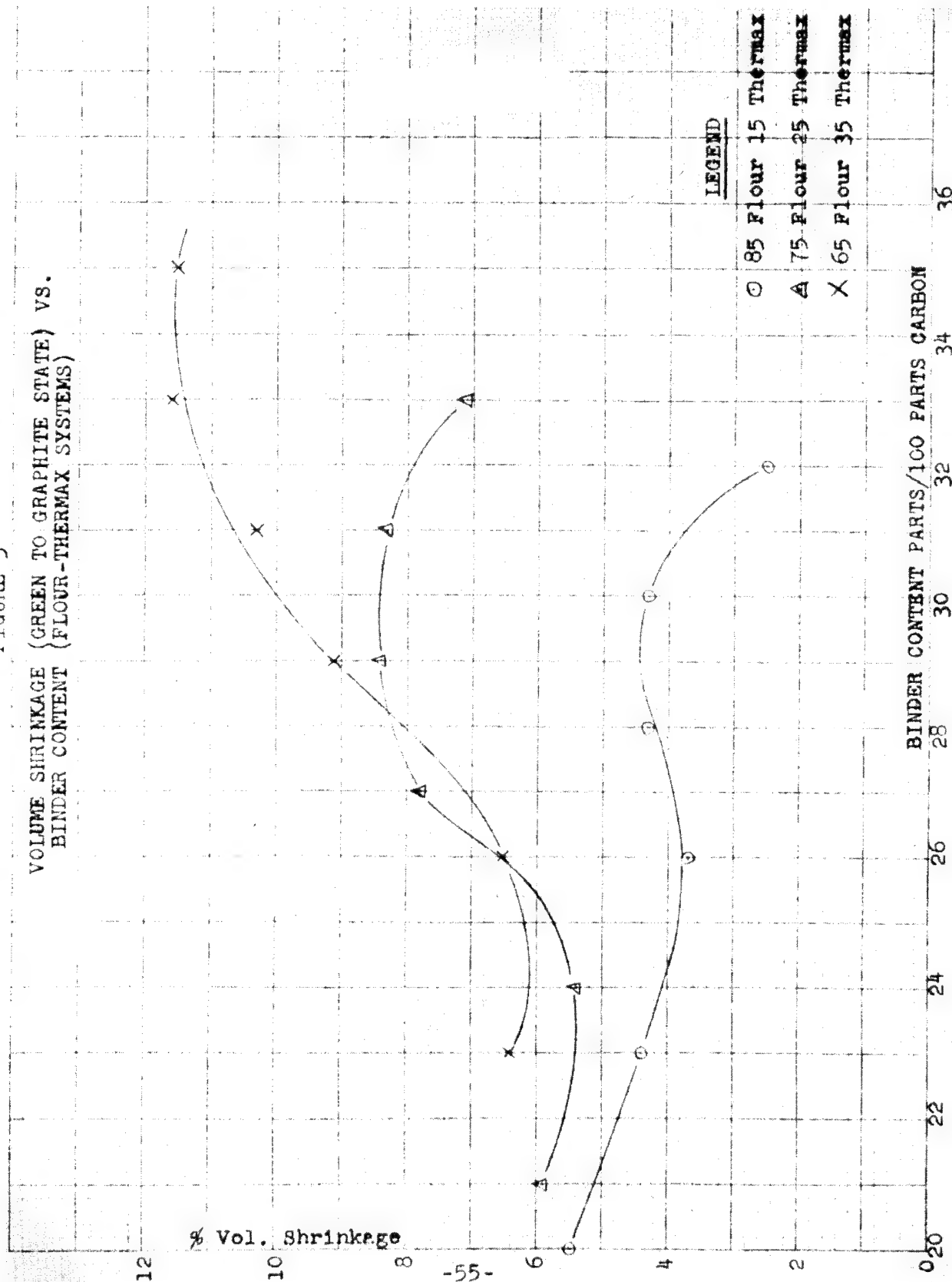


FIGURE 6  
 VARIATIONS OF APPARENT DENSITY WITH PARTS THERMAX (GRAPHITE STATE)  
 (AT OPTIMUM BINDER CONTENT)

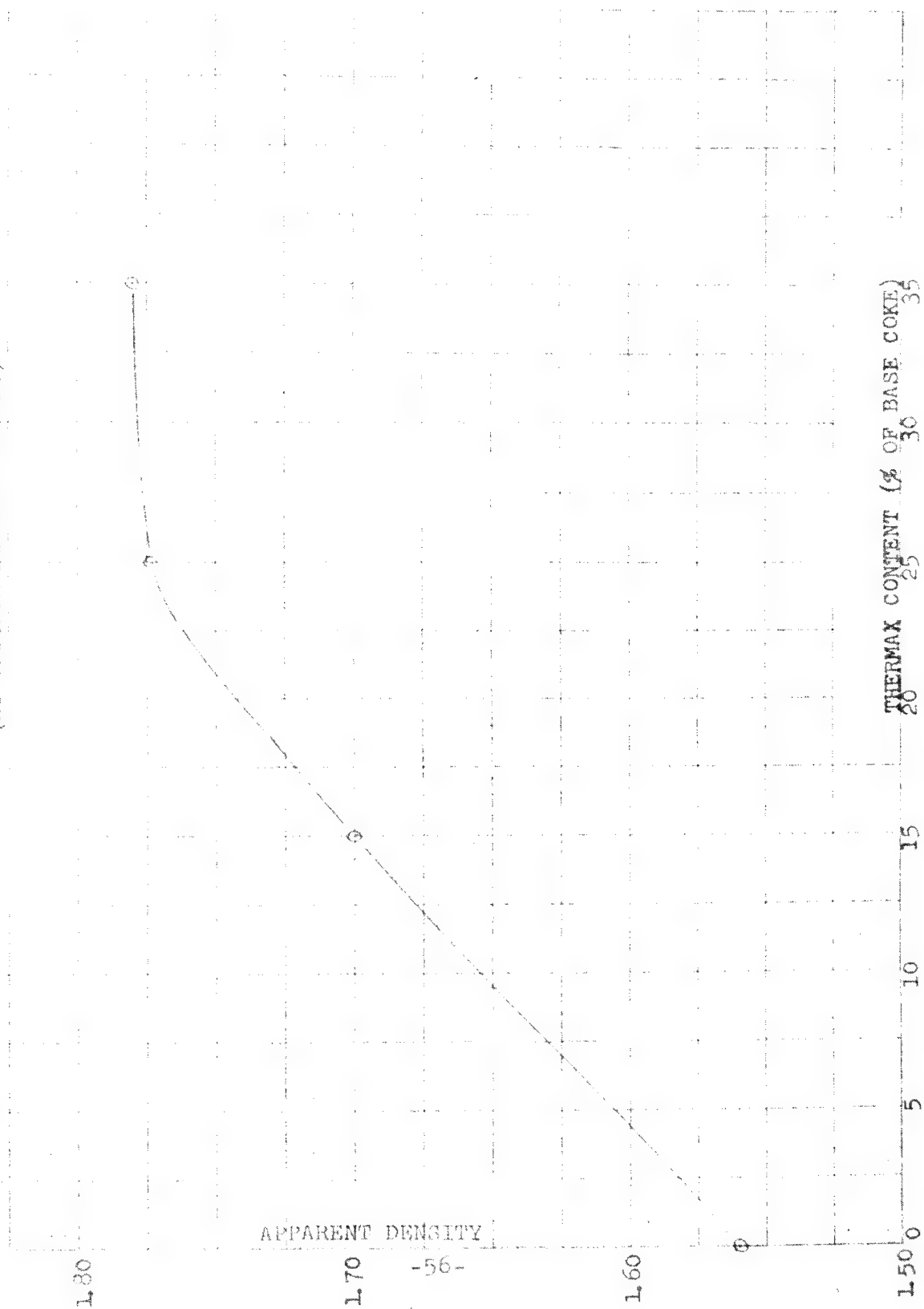


FIGURE 7

VARIATIONS OF APPARENT DENSITY WITH BINDER CONTENT  
(100% FLOUR SYSTEMS)

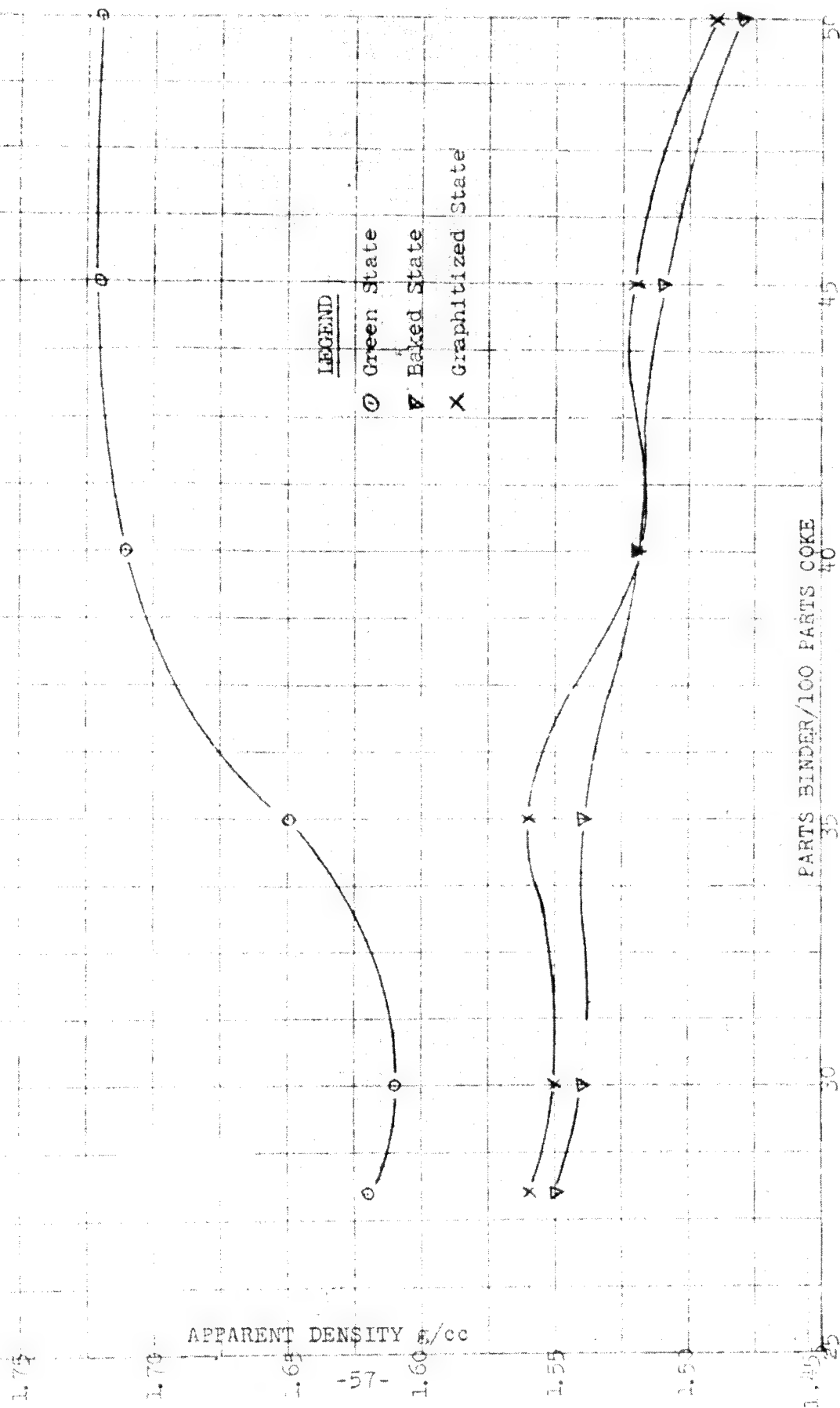
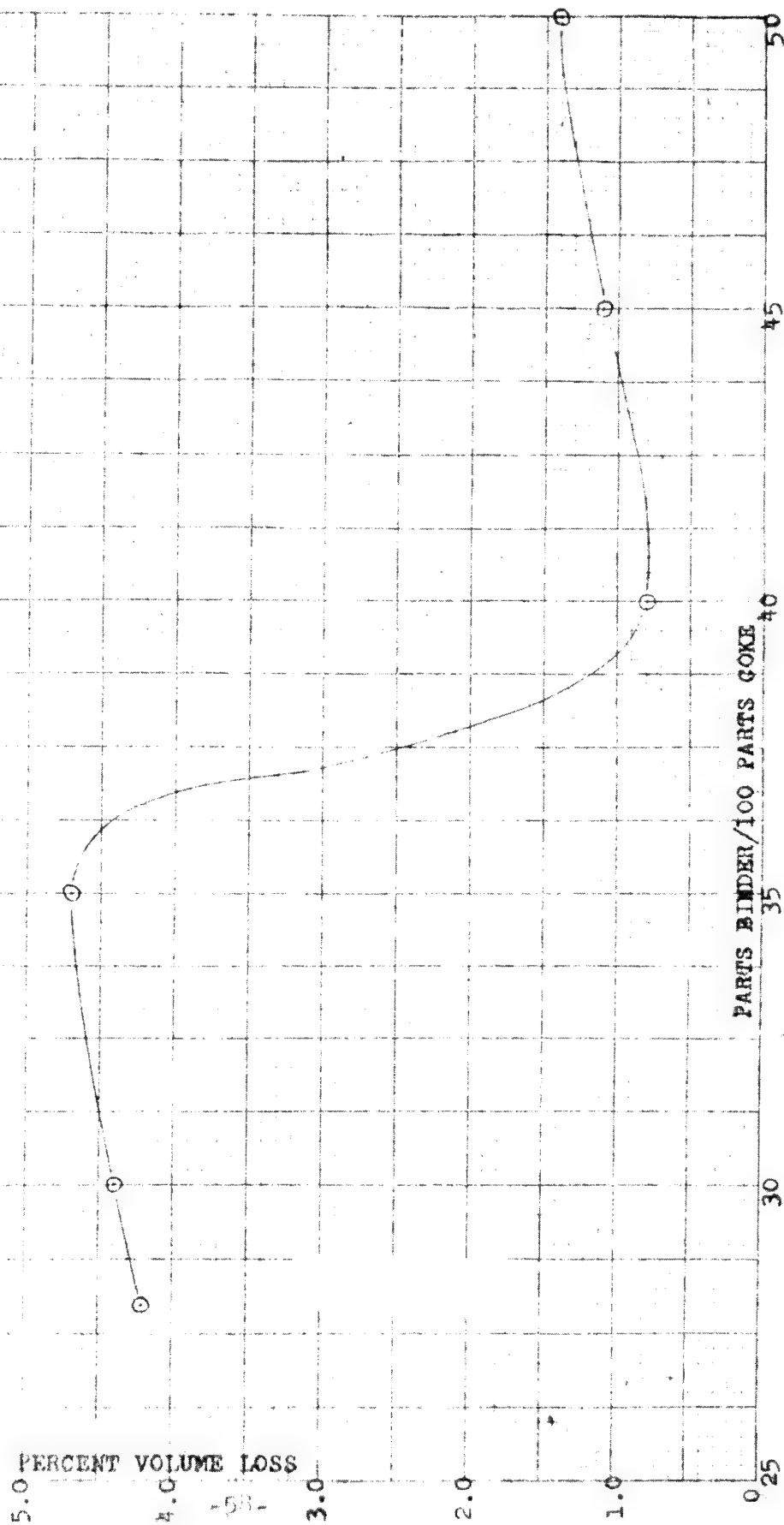


FIGURE 8

VARIATIONS IN VOLUMETRIC SHRINKAGE WITH BINDER CONTENT  
IN 100% COKE FLOUR SYSTEMS (GREEN STATE TO GRAPHITE STATE)



**FIGURE 9**

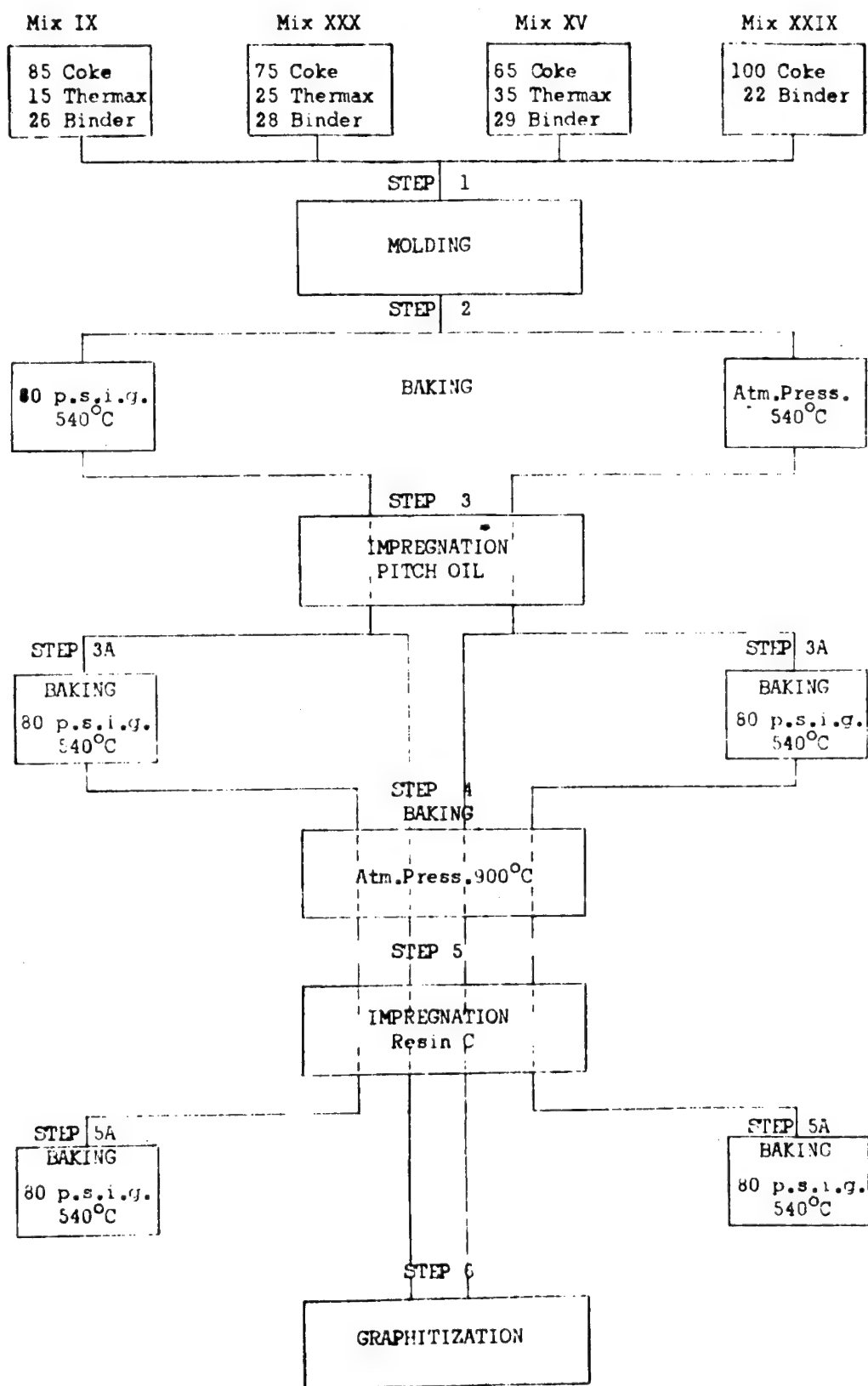


FIGURE 10

GROUP 1

GROUP 2

GROUP 3

GROUP 4

STEP 1 GREEN				STEP 1 GREEN				STEP 1 GREEN				STEP 1 GREEN			
Mixes	A.D. (Av.)			Mixes	A.D. (Av.)			Mixes	A.D. (Av.)			Mixes	A.D. (Av.)		
IX	1.77			IX	1.77			IX	1.77			IX	1.77		
XV	1.78			XV	1.78			XV	1.78			XV	1.78		
XXIX	1.55			XXIX	1.55			XXIX	1.55			XXIX	1.55		
XXX	1.75			XXX	1.79			XXX	1.79			XXX	1.79		

STEP 2 BAKE				STEP 2 BAKE				STEP 2 BAKE				STEP 2 BAKE			
Atm. Press.	A.D.	AV	CRB	80 p.s.i.g.	A.D.	AV	CRB	80 p.s.i.g.	A.D.	AV	CRB	80 p.s.i.g.	A.D.	AV	CRB
Mixes	1.65	+0.5	70.0	Mixes	1.69	+0.7	80.3	Mixes	1.69	+0.3	80.8	Mixes	1.65	+0.5	70.7
IX	1.65			IX	1.72	-1.2	79.6	IX	1.73	-1.3	80.6	IX	1.65		
XV	1.89	-2.3	64.0	XXIX	1.49	+1.7	85.8	XV	1.72	-1.2	79.6	XV	1.69	-2.6	62.2
XXIX	1.49	+1.0	34.3	XXX	1.72	-1.2	78.2	XXIX	1.49	+1.7	86.8	XXIX	1.49	+0.9	84.9
XXX	1.71	-2.3	69.5	XXX	1.72	-1.2	78.2	XXX	1.72	-0.7	80.0	XXX	1.70	-2.0	69.4

STEP 3 IMPERGATION				STEP 3 IMPERGATION				STEP 3 IMPERGATION				STEP 3 IMPERGATION			
Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.
IX	9.9	72	1.81	IX	7.1	60	1.81	IX	5.7	57	1.80	IX	9.5	69	1.81
XV	6.9	61	1.81	XV	3.1	36	1.77	XV	2.2	25	1.77	XV	7.0	62	1.81
XXIX	18.4	84	1.76	XXIX	18.7	82	1.77	XXIX	18.2	81	1.76	XXIX	18.4	84	1.76
XXX	6.3	80	1.82	XXX	5.0	52	1.81	XXX	4.7	48	1.80	XXX	6.7	56	1.81

STEP 3A BAKE				STEP 3A BAKE				STEP 3A BAKE				STEP 3A BAKE			
80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.
Mixes	1.76	-1.2	50	Mixes	1.77	-1.1	61	Mixes	1.78	-2.1	42	Mixes	1.75	-1.2	47
IX	1.76			IX	1.77			IX	1.78			IX	1.75		
XV	1.81	-4.7	57	XV	1.75	57		XV	1.79	-4.1	17	XV	1.78	-4.6	36
XXIX	1.69	-1.9	49	XXIX	1.67	67		XXIX	1.61	-0.5	33	XXIX	1.62	-1.7	30
XXX	1.73	-4.3	44	XXX	1.75	53		XXX	1.73	-3.3	33	XXX	1.73	-4.4	40

STEP 4 BAKE				STEP 4 BAKE				STEP 4 BAKE				STEP 4 BAKE			
Atm. Press.	A.D.	AV	Imp. Res.	Atm. Press.	A.D.	AV	Imp. Res.	Atm. Press.	A.D.	AV	Imp. Res.	Atm. Press.	A.D.	AV	Imp. Res.
Mixes	1.76	-1.2	50	Mixes	1.79	-1.1	48	Mixes	1.78	-2.1	42	Mixes	1.75	-1.2	47
IX	1.76			IX	1.79			IX	1.78			IX	1.75		
XV	1.81	-4.7	57	XV	1.78	-3.9	29	XV	1.79	-4.1	17	XV	1.78	-4.6	36
XXIX	1.69	-1.9	49	XXIX	1.69	-1.1	59	XXIX	1.61	-0.5	33	XXIX	1.62	-1.7	30
XXX	1.73	-4.3	44	XXX	1.80	-3.6	36	XXX	1.73	-3.3	33	XXX	1.73	-4.4	40

STEP 5 IMPERGATION				STEP 5 IMPERGATION				STEP 5 IMPERGATION				STEP 5 IMPERGATION			
Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.	Mixes	Wt. Gain	% Voids Filled	A.D.
IX	6.2	87	1.87	IX	5.3	81	1.88	IX	5.3	81	1.88	IX	2.7	37	1.81
XV	3.3	58	1.87	XV	3.9	63	1.86	XV	3.9	63	1.86	XV	4.9	77	1.87
XXIX	10.1	97	1.86	XXIX	13.6	98	1.83	XXIX	13.6	98	1.83	XXIX	13.4	97	1.84
XXX	4.2	73	1.87	XXX	3.2	55	1.85	XXX	3.2	55	1.85	XXX	1.8	32	1.83

STEP 5A BAKE				STEP 5A BAKE				STEP 5A BAKE				STEP 5A BAKE			
80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.	80 p.s.i.g.	A.D.	AV	Imp. Res.
Mixes	1.81	-4.0	47.0	Mixes	1.82	37.4		Mixes	1.82	37.4		Mixes	1.81	-4.3	
IX	1.81			IX	1.82			IX	1.82			IX	1.81		
XV	1.83	36.1		XV	1.81	27.3		XV	1.81	27.0		XV	1.91	-6.9	
XXIX	1.78	54.9		XXIX	1.76	51.2		XXIX	1.73	54.2		XXIX	1.73	-3.9	
XXX	1.83	41.2		XXX	1.82	29.7		XXX	1.73	54.2		XXX	1.86	-4.2	

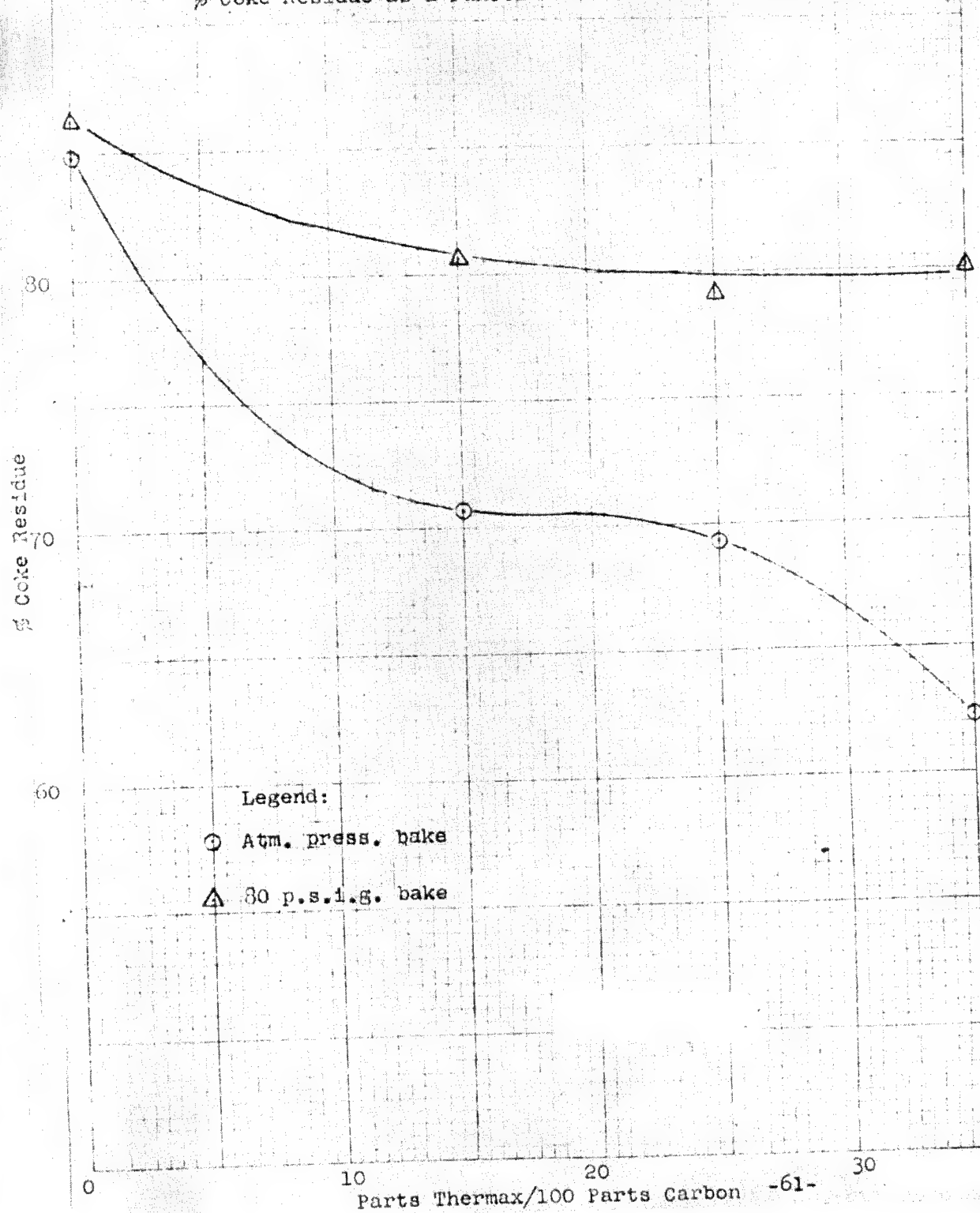
STEP 6 GRAPHITIZATION				STEP 6 GRAPHITIZATION				STEP 6 GRAPHITIZATION				STEP 6 GRAPHITIZATION			
Mixes	A.D.	AV	Imp. Res.	Mixes	A.D.	AV	Imp. Res.	Mixes	A.D.	AV	Imp. Res.	Mixes	A.D.	AV	Imp. Res.
IX	1.81	-4.3		IX	1.84	-3.2		IX	1.84	-3.2		IX	1.81	-4.3	
XV	1.91	-6.9		XV	1.86	-4.9		XV	1.86	-4.9		XV	1.91	-6.9	
XXIX	1.73	-3.9		XXIX	1.79	-3.9		XXIX	1.79	-3.9		XXIX	1.73	-3.9	
XXX	1.86	-4.2		XXX				XXX				XXX	1.86	-4.2	

\* CRB - Binder Coke Residue  
 \*\* Imp. Res. - Carbon Residue from impregnant



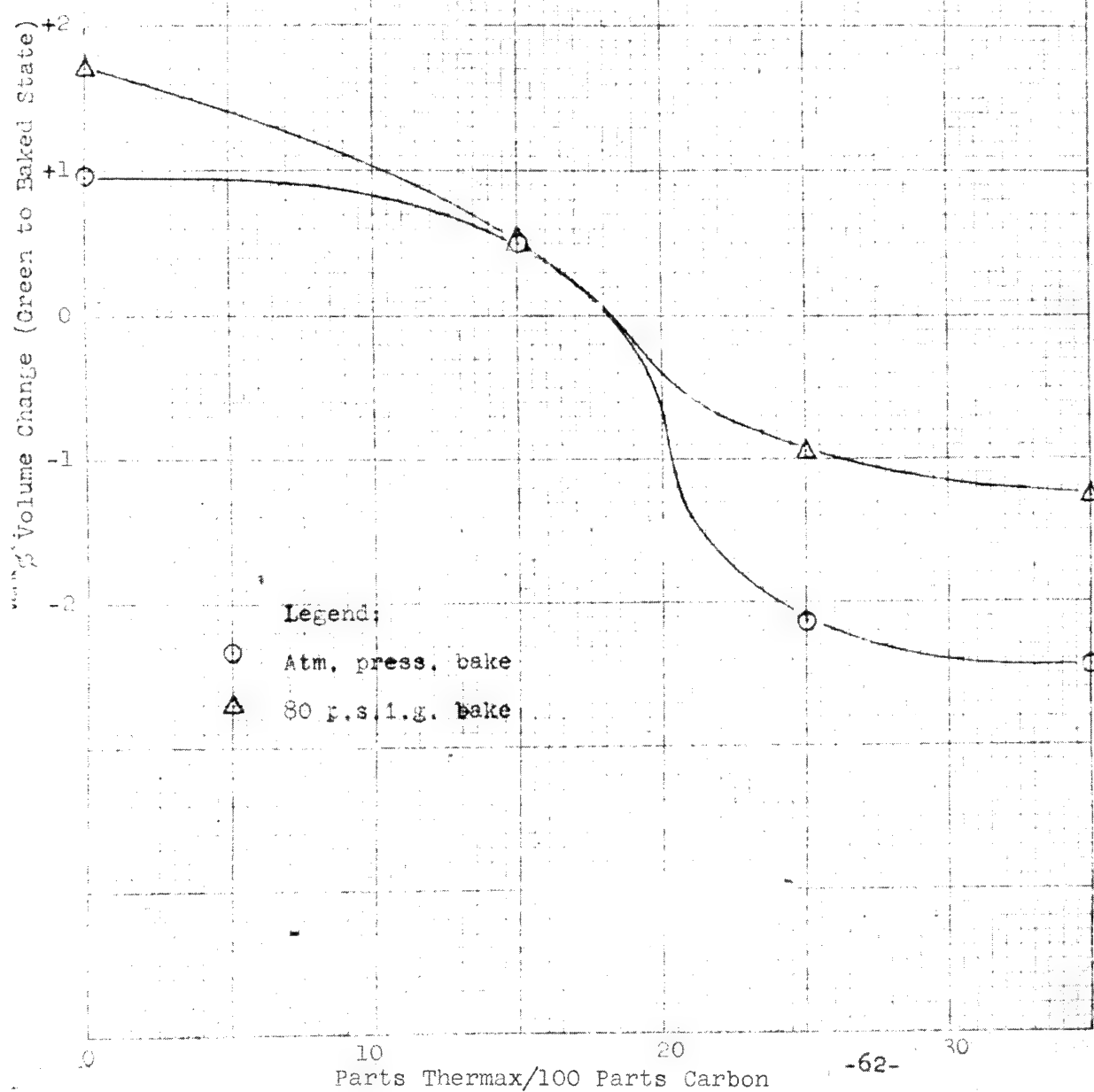
FIGURE 11

% Coke Residue as a Function of Thermax Concentration

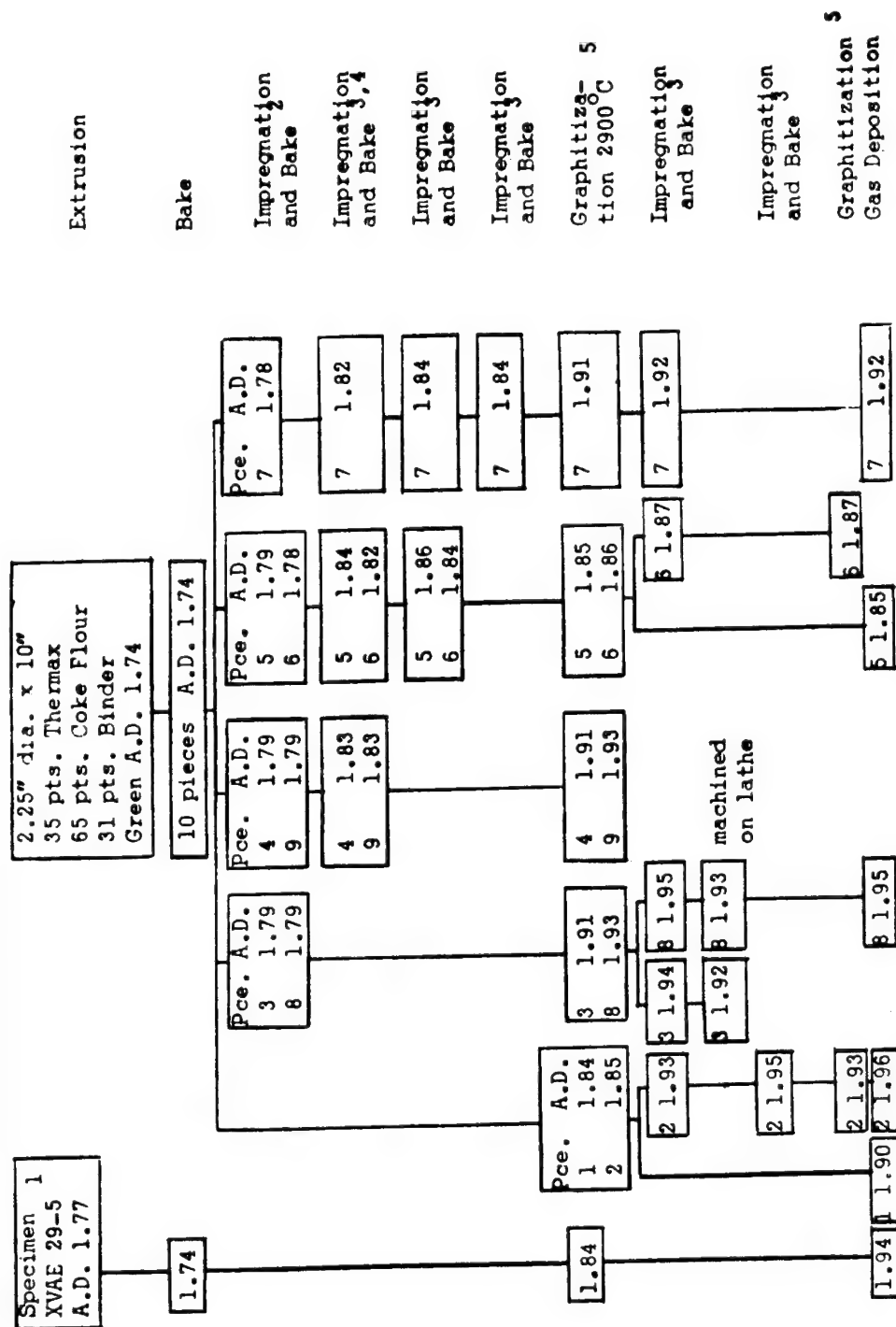


**FIGURE 12**

% Volume Change as a Function of Thermax Concentration



FLOW DIAGRAM FOR THE PREPARATION OF HIGH DENSITY GRAPHITE FROM CALCINED  
PETROLEUM COKE FLOUR, THERMAX AND COAL TAR PITCH BINDER  
(XVE 31 MIX)



1. 35 pts. Thermax, 65 pts. Coke Flour, 1/2 pt. polyvinylchloride, 29 pts. binder.
2. Atmospheric Bake, 850° C.
3. Pressure bake (6 atm.) to 540° C, atmospheric bake to 850° C.
4. Specimens 4 and 9 were baked at atmospheric pressure without packing.
5. Specimens 1, 2, 7 at upheat rate of 1°/min., 5 and 6 at 2°/min., 3, 4, 8, 9 at 1/2° per min. between 1200° and 2200° C.
6. Specimen 4 to 2100° C.

FIGURE 14

FLOW DIAGRAM FOR THE PREPARATION OF HIGH DENSITY GRAPHITE  
FROM CALCINED PETROLEUM COKE FLOUR AND COAL TAR PITCH BINDER (XXIX E 36 MIX)

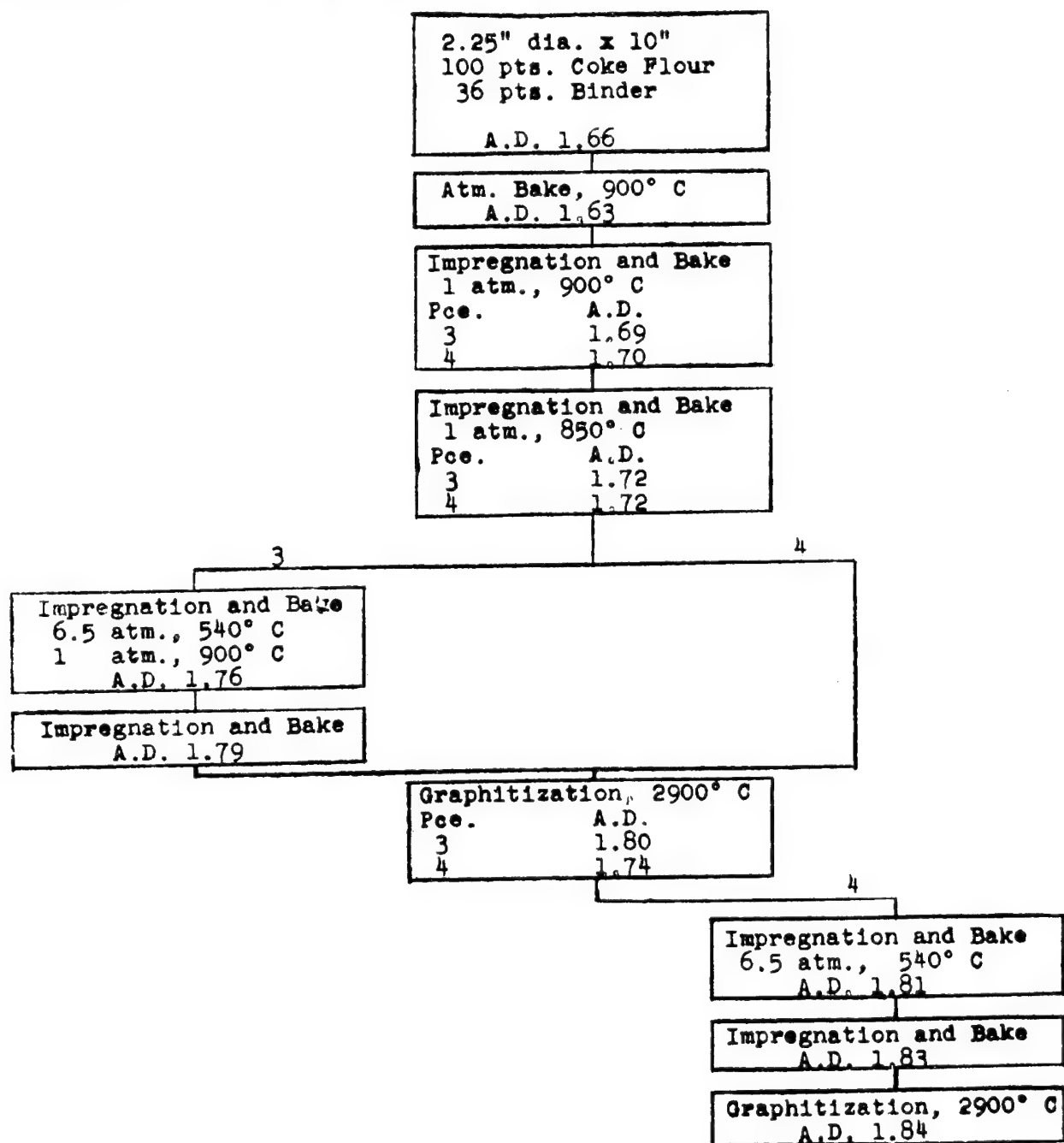
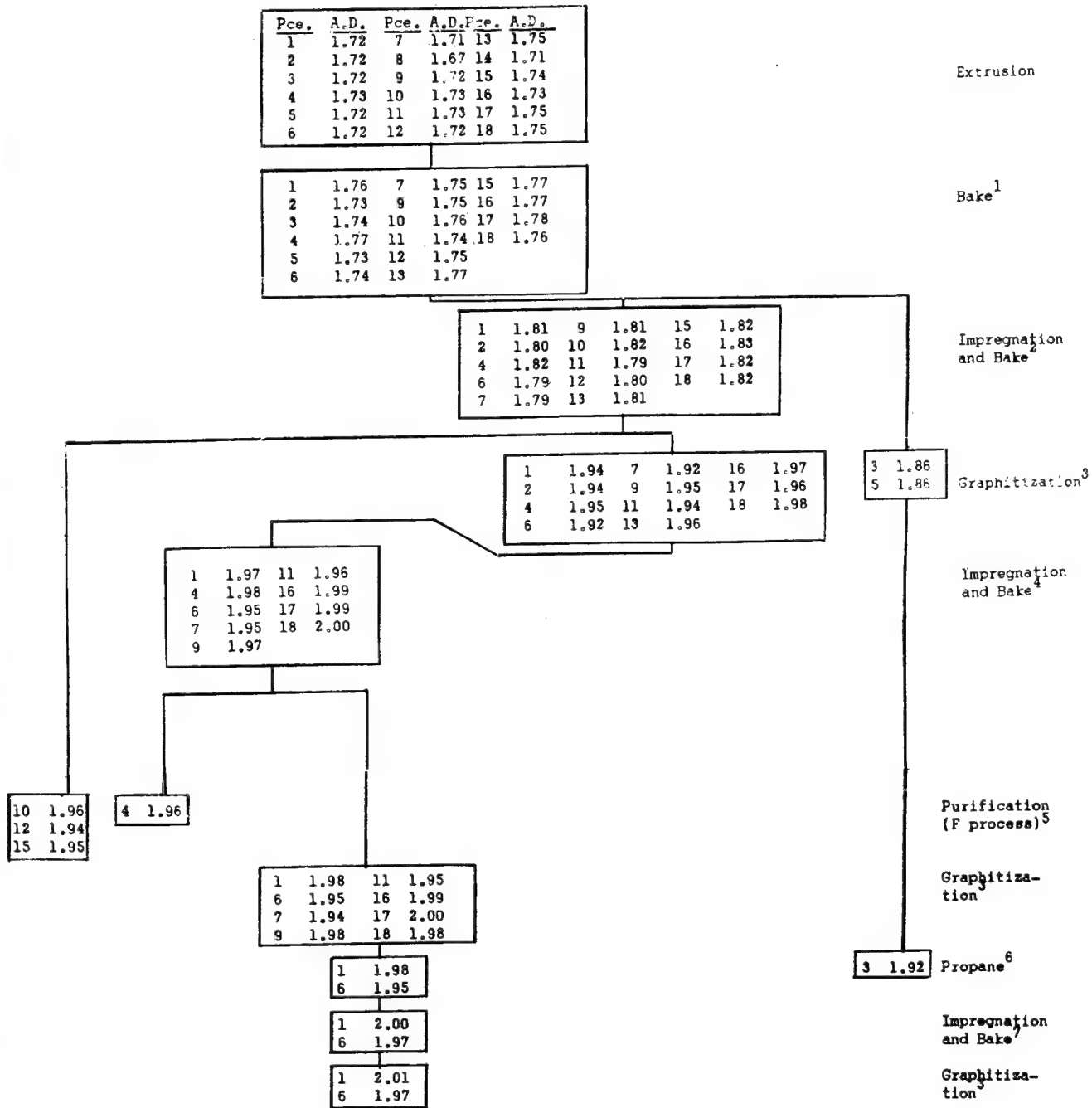


FIGURE 15

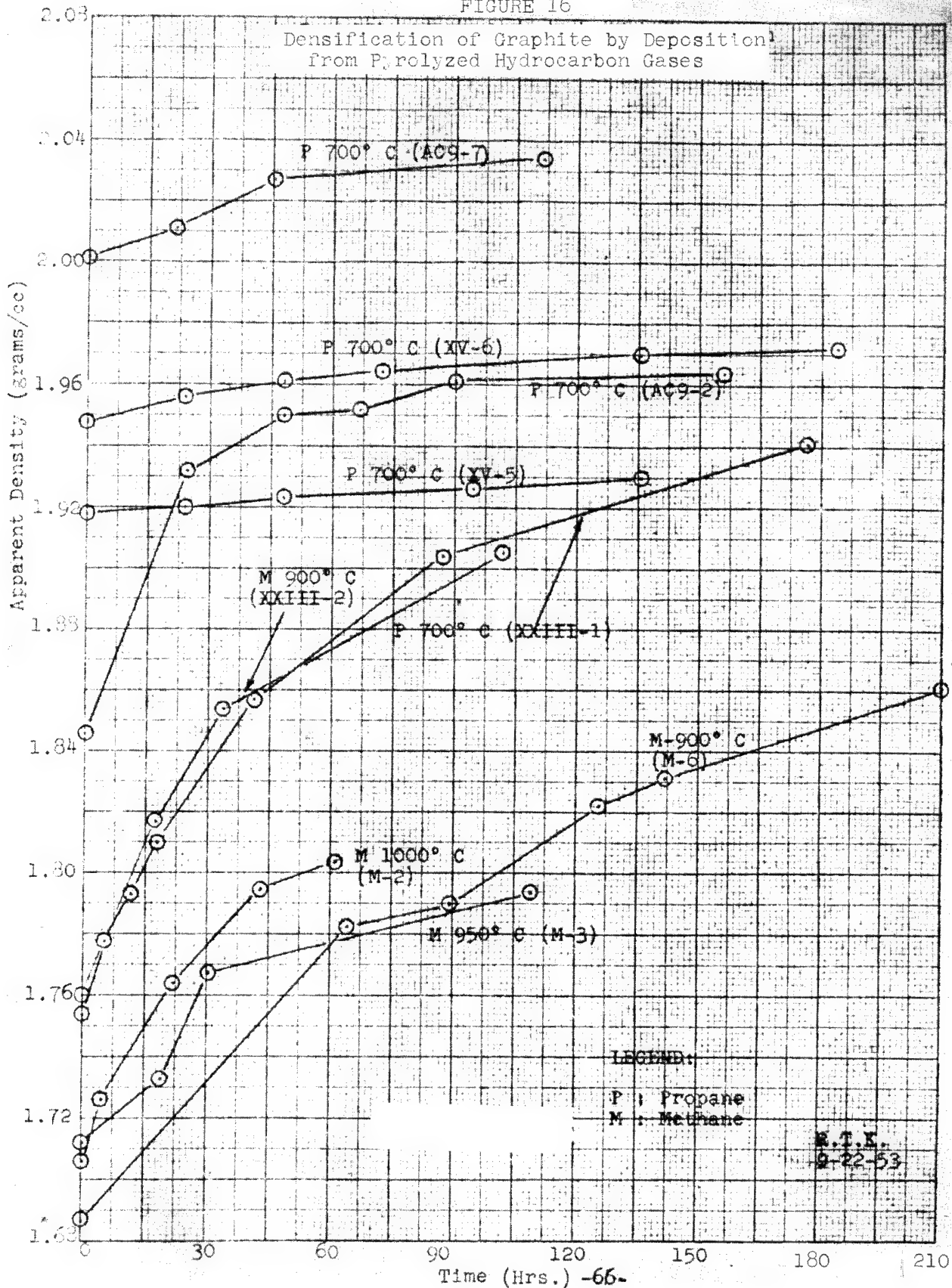
PROCESSING OF EXTRUDED STOCK FROM THERMAX, CALCINED COKE FLOUR, AND COAL TAR PITCH BINDER  
(XV F B 31 MIX)



1. Atmospheric bake to 900°C.
2. Impregnant: Resin C — Atmospheric bake to 540°C (some specimens to 760°C)
3. To 2900°. Schedule: 700° - 1300°C: 1°/min. 1300°C - 2100°C: 0.5°/min. 2100° - 2900°C: 1°/min.
4. Impregnant: Resin C. Atmospheric bake to 540° C except pressure bake (80 psig) for specimens 1 and 4.
5. To 2500°C.
6. Specimens 1 and 6 for 24 hours, specimen 3 for 10 days.
7. Impregnant: Resin C - Pressure Bake to 540° C.

FIGURE 16

Densification of Graphite by Deposition  
from Pyrolyzed Hydrocarbon Gases



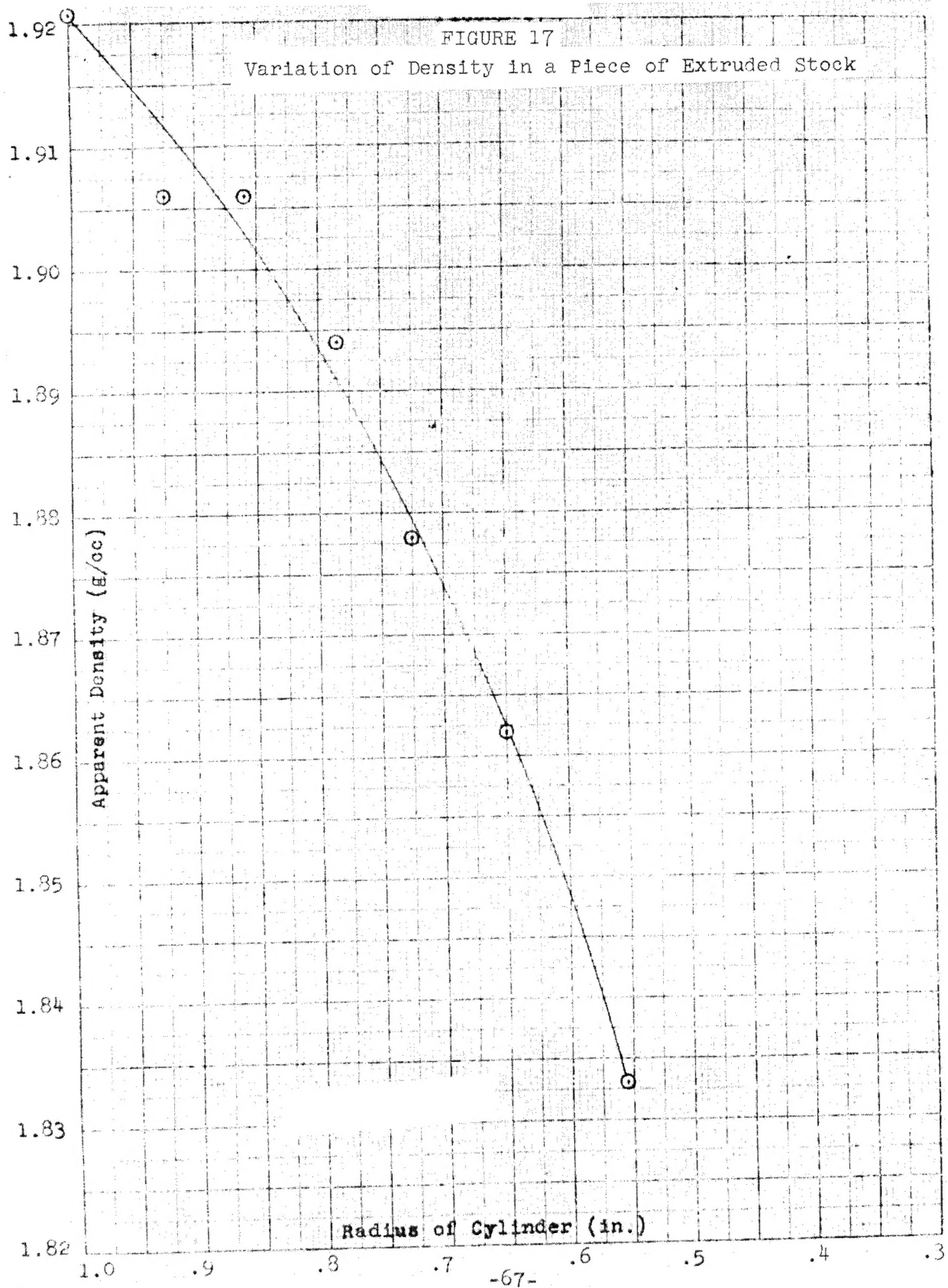


FIGURE 18

Elastic Modulus of Extruded Stock of Different Densities

- Graphitized, impregnated, regraphitized.
- Green.
- Graphitized.
- △ Baked, impregnated, rebaked.
- × Baked.

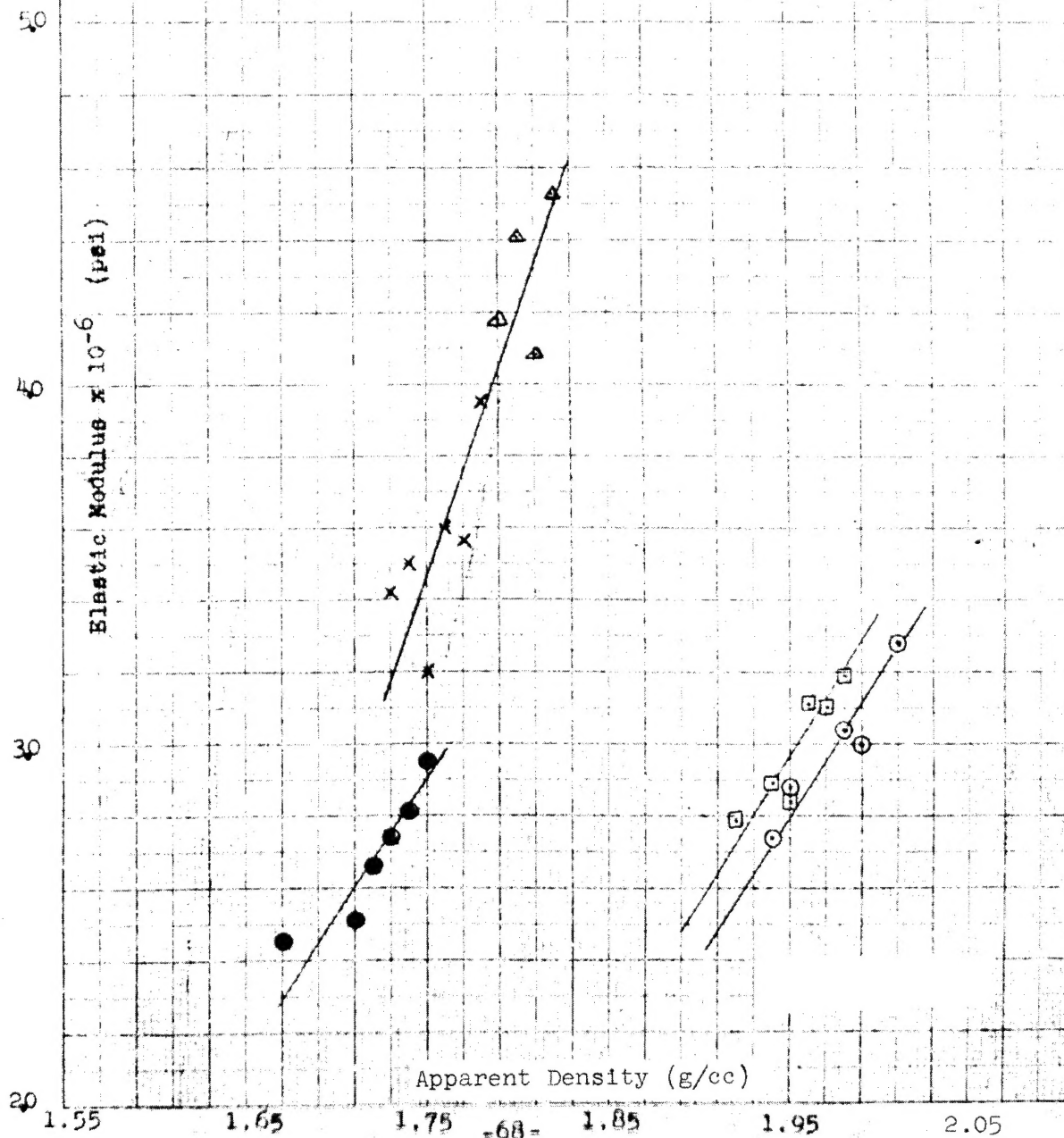




FIGURE 5

VOLUME SHRINKAGE (GREEN TO GRAPHITE STATE) VS.  
BINDER CONTENT (FLOUR-THERMAX SYSTEMS)

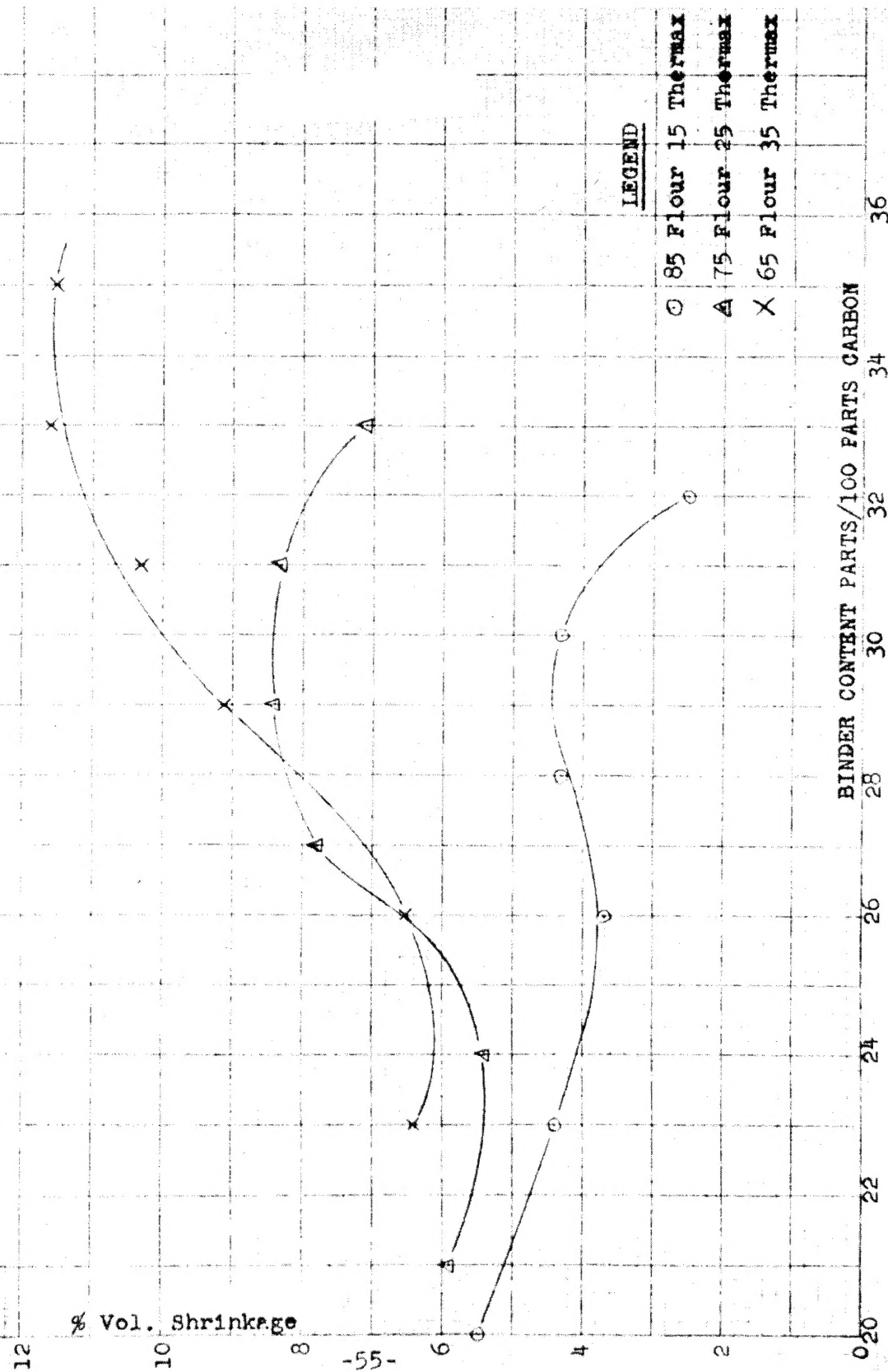


FIGURE 6

VARIATIONS OF APPARENT DENSITY WITH PARTS THERMAX (GRAPHITE STATE)  
(AT OPTIMUM BINDER CONTENT)

